

99361

APPENDIX D
SAS REQUEST FORMS

**Contract Lab Program
SAS Parameters**

Drinking Water

Organics (low detection limits)
Inorganics (low detection limits)
Additional Pesticides
Chloride, Sulfate
Acidity, alkalinity, pH
Nitrate - nitrite

Ground Water and Leachate

Total Organic Carbon
Additional Pesticides
Sulfate, chloride
Acidity, alkalinity, pH
Nitrate - nitrite
BOD, COD
Ammonia
TKN
Phosphorus (total)

Surface Water

TDS
TSS
Alkalinity, acidity, pH
Sulfate, chloride
Nitrate - nitrite
Phosphorus (total)

Soil

Dioxin
Additional pesticides
Total Organic Carbon

Sediment

Additional Pesticides
~~Hexavalent Chromium~~
Total Organic Carbon

Lagoon Waste

Dioxin
Additional Pesticides
Incineration Parameters

DRINKING WATER SAS REQUESTS

U.S. ENVIRONMENTAL PROTECTION AGENCY
CLP Sample Management Office
P.O. Box 818, Alexandria, Virginia 223113
PHONE: (703)557-2490 or FTS/557-2490

SPECIAL ANALYTICAL SERVICES
Client Request

☒ Regional Transmittal ☐ Telephone Request

A. EPA Region/Client: Region V WW Engineering & Science

B. RSCC Representative: Jan Pels

C. Telephone Number: (312) 353-2720

D. Date of Request: _____

E. Site Name: Skinner Landfill - West Chester, OH

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. General description of analytical service requested: _____
Organics - Drinking water with low level detection limits, and low level methylene chloride requirements.
2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium, or high concentration):
Twenty-four (24) drinking water samples, including duplicates and spikes. Whole solid samples assumed.
3. Purpose of analysis (specify whether Superfund (Remedial or Enforcement), RCRA, NPDES, etc.):
Superfund - Remedial Action

4. Estimated date(s) of collection: _____
5. Estimated date(s) and method of shipment: _____
Daily by overnight carrier.
6. Number of days analysis and data required after laboratory receipt of samples:
Laboratory should report results within 30 days after receipt of samples.
7. Analytical protocol required (attach copy if other than a protocol currently used in this program):
CLP SOW for Organic Analysis (Multi-Media, Multi-Concentration), 8/87.
8. Special technical instructions (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):
1. Modifications to the CLP Organic SOW 8/87 in Attachment I.
2. Required low level quantitation limits in Attachment II.
3. Methylene chloride: CAS Number 75-09-2. As per CLP Organics SOW 8/87 with the following modifications: the laboratory is required to demonstrate that the laboratory blank/method samples do not contain methylene chloride at concentrations greater than the required detection limits prior to or in between sample analysis. If this criteria is not met, correction action shall be taken fore the sample analyses begin.
9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.). If not completed, format of results will be left to program discretion.
As per CLP Organics SOW 8/87 with modifications as outlined in Attachment I.
10. Other (use additional sheets or attach supplementary information, as needed):

11. Name of sampling/shipping contact: Bob Phillips
Phone: (616) 942-9600 ext. 263

12. Data Requirements

Parameter	Detection Limit	Precision Desired (Percent or Concentration)
<u>Methylene Chloride</u>	<u>1 ug/l</u>	<u>± 20%</u>
<u>See Attachment II</u>	<u>See Attachment II</u>	<u>±20%</u>
<u> </u>	<u> </u>	<u> </u>
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13. QC Requirements

Audits Required	Frequency of Audits	Limits (Percent or Concentration)
<u>As per CLP Organic SOW 8/87</u>	<u>As per CLP Organic SOW 8/87</u>	<u>Exceptions to CLP Organic SOW 8/87.</u>
<u> </u>	<u> </u>	<u>(see attachment)</u>
<u> </u>	<u> </u>	<u> </u>
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<u> </u>	<u> </u>	<u> </u>

14. Action Required if Limits are Exceeded

Take corrective action and repeat analysis.

Contact Region V RSCC Jan Pels (312) 353-2720 or

Chuck Elly (312) 353-9087

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for special analytical services. Should you have any questions or need any assistance, please contact your Regional representative at the Sample Management Office.

U.S. ENVIRONMENTAL PROTECTION AGENCY
CLP Sample Management Office
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Methylene Chloride

SPECIAL ANALYTICAL SERVICES
Client Request

☒ Regional Transmittal ☐ Telephone Request

A. EPA Region/Client: Region V WW Engineering & Science
B. RSCC Representative: Jan Pels
C. Telephone Number: (312) 353-2720
D. Date of Request: October-December, 1989
E. Site Name: Skinner Landfill - West Chester, OH

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. General description of analytical service requested:

Analysis of soil and water using RAS and SAS analysis. SAS analysis for methylene chloride shall demonstrate that the laboratory blank/method blank samples do not contain methylene chloride.

2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium, or high concentration):

Thirty-nine (39) groundwater, 5 leachate, 48 surface water, 48 sediment, and 80 soil samples. Low to medium concentration. Included duplicates and blanks.

3. Purpose of analysis (specify whether Superfund (Remedial or Enforcement), RCRA, NPDES, etc.):

Superfund - Remedial Action

4. Estimated date(s) of collection: _____
October-December, 1989
5. Estimated date(s) and method of shipment: _____
Daily by overnight carrier.
6. Number of days analysis and data required after laboratory receipt of samples:
Laboratory should report results within 30 days after receipt of samples
7. Analytical protocol required (attach copy if other than a protocol currently used in this program):
As per CLP SOW for Organic Analysis (Multi-Media, Multi-Concentration) SOW 8/87 for analysis of methylene chloride. SAS methylene chloride sample should be sent to assigned RAS organics laboratory.
8. Special technical instructions (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):
Methylene chloride: CAS Number 75-09-2. As per CLP Organics SOW 8/87 with the following modifications: the laboratory is required to demonstrate that the laboratory blank/method blank samples do not contain methylene chloride at concentrations greater than the required detection limits, prior to or in between sample analysis. If this criteria is not met, corrective action shall be taken before the sample analyses begin.
9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.). If not completed, format of results will be left to program discretion.
As per CLP Organics SOW 8/87.
10. Other (use additional sheets or attach supplementary information, as needed):

11. Name of sampling/shipping contact: Bob Phillips
Phone: (616) 942-9600 ext. 263

12. Data Requirements

Parameter	Detection Limit	Precision Desired (Percent or Concentration)
<u>Methylene chloride</u>		
<u>in water</u>	<u>5 ug/l</u>	<u>80-120%</u>
<u>in water</u>	<u>5 ug/kg</u>	<u>80-120%</u>

13. OC Requirements

Audits Required	Frequency of Audits	Limits (Percent or Concentration)
as per CLP Organics	SOW 8/87	

14. Action Required if Limits are Exceeded

Take corrective action and repeat analysis.
Contact Region V RSCC Jan Pels (312) 353-2720 or
Chuck Elly (312) 353-9087

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for special analytical services. Should you have any questions or need any assistance, please contact your Regional representative at the Sample Management Office.

U.S. ENVIRONMENTAL PROTECTION AGENCY
CLP Sample Management Office
P.O. Box 818, Alexandria, Virginia 223113
PHONE: (703)557-2490 or FTS/557-2490

Waste Samples
Additional Pesticides

SPECIAL ANALYTICAL SERVICES
Client Request

☒ Regional Transmittal ☐ Telephone Request

A. EPA Region/Client: Region V WW Engineering & Science
B. RSCC Representative: Jan Pels
C. Telephone Number: (312) 353-2720
D. Date of Request: _____
E. Site Name: Skinner Landfill - West Chester, OH

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. General description of analytical service requested:

High hazard waste sample analysis of seven chlorinated hydrocarbon compounds: 3 which are currently TCL compounds, 4 which are not, using SAS 3900-I protocol (see Table 1). Analysis by GC/MS method per SAS 3900-I. Standards may be difficult to obtain. Contact EPA Pesticide Repository. Laboratory should perform preparation and analysis only for extractable fraction, which includes pesticides.

2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium, or high concentration):

58 High hazard waste samples. Whole solid samples assumed. Includes duplicates.

3. Purpose of analysis (specify whether Superfund (Remedial or Enforcement), RCRA, NPDES, etc.):

Superfund - Remedial Action

12. Data Requirements

Parameter	Detection Limit	Precision Desired (Percent or Concentration)
Chlordene	20 mg/kg	plus/minus 35%
Hexachloronorboradiene	20 mg/kg	plus/minus 35%
1,2,3,4,5,7,7. Hepta- chloronorborene	20 mg/kg	plus/minus 35%
Octachlorocyclopentene	20 mg/kg	plus/minus 35%
Hexachlorobutadiene	20 mg/kg	plus/minus 35%
Hexachlorobenzene	20 mg/kg	plus/minus 35%
Hexochloroboradiene	20 mg/kg	plus/minus 35%

13. OC Requirements

Audits Required	Frequency of Audits	Limits (Percent or Concentration)
as per SAS 3900-I	as per SAS 3900-I	plus/minus 35%

14. Action Required if Limits are Exceeded

As per SAS 3900-I.
Contact Region V RSCC Jan Pels (312) 353-2720 or
Chuck Elly (312) 353-9087

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for special analytical services. Should you have any questions or need any assistance, please contact your Regional representative at the Sample Management Office.

U.S. Environmental Protection Agency
CLP Sample Management Office
P. O. Box 818, Alexandria, Virginia 22313
PHONE: (703)/557-2490 or FTS/557-2490

SAS Number

SPECIAL ANALYTICAL SERVICES
Client Request

☒

Regional Transmittal



Telephone Request

A. EPA Region/Client: Region V WW Engineering & Science
B. RSCC Representative: Jan Pels
C. Telephone Number: 312/353-2720
D. Date of Request: _____
E. Site Name: Skinner Landfill - West Chester, Ohio

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. General description of analytical service requested: Analysis of drinking water/
residential wells for hexachloronorboradiene, octachlorocyclopentene, chlordene,
heptachloronorborene by the detection limit modification of CLP SOW 8/87.
Standards may be difficult to obtain (check with EPA Pesticide Repository).

2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium, or high concentration):

24 drinking water samples including duplicates and blanks.

Whole aqueous samples of low concentration are assumed.

Includes duplicates and spikes.

Purpose of analysis (specify whether Superfund (Remedial or Enforcement), RCRA, NPDES, etc.):

Superfund - Remedial Action

4. Estimated date(s) of collection: _____
5. Estimated date(s) and method of shipment: Daily by overnight carrier.
6. Number of days analysis and data required after laboratory receipt of samples:
Laboratory should report results within 30 days after receipt of samples.

7. Analytical protocol required (attach copy if other than a protocol currently used in this program):

CLP SOW for Organic Analysis (Multi-Media, Multi-Concentration) 8/87. Analyze
using GC/ECP according to SOW for pesticides. For samples that are greater than
requested GC/MS detection limits, analyze according to SOW for BW fraction.

8. Special technical instruction (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):

1. Modification to the CLP Organic SOW 8/87 in Attachment I.
2. Required low level quantitation limits in Attachment II. Perform method detection
limit study as per 40 CFR 136, Appendix B. Conduct calibrations and QA/QC (using
chlordene, octachlorocyclopentene, heptachloronorborene, and heptachloronorboreadiene.)

9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.). If not completed, format of results will be left to program discretion.

As per CLP Organics SOW 8/87 with modifications as outlined in Attachment I.

10. Other (use additional sheets or attach supplementary information, as needed):

11. Name of sampling/shipping contact: Bob Phillips

Phone: 616/ 942-9600 EXT 263

3.

I. DATA REQUIREMENTS

<u>Parameter:</u>	<u>Detection Limit</u>	<u>Precision Desired</u> (+/- % or Conc.)
<u>see Attachment II</u>	<u>see Attachment II</u>	<u>+ 20%</u>
<u> </u>	<u> </u>	<u> </u>
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II. QC REQUIREMENTS

<u>Audits Required</u>	<u>Frequency of Audits</u>	<u>Limits* (% or Conc.)</u>
<u>as per CLP Organics</u> <u>SOW 8/87</u>	<u>as per CLP Organics</u> <u>SOW 8/87</u>	<u>exceptions to CLP</u> <u>Organics SOW 8:87;</u> <u>see Attachment I</u>
<u> </u>	<u> </u>	<u> </u>
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III. ACTION REQUIRED IF LIMITS ARE EXCEEDED:

Contact Region V RSCC: Jan Pels 312/ 353-2720 or Chuck Elly 312/ 353-9087

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for special analytical services. Should you have any questions or need any assistance, please call the Sample Management Office.

ATTACHMENT I

MODIFICATION TO THE CLP ORGANICS SOW 8/87 FOR THE REGION V RESIDENTIAL WELL SAS

SEMI-VOLATILES ANALYSIS

- a) Extraction/Blowdown: Extract entire liter bottle, rinsing cap and bottle, and add to sample. Final blowdown volume may be decreased to 0.5 ml to achieve required detection limits.
- b) Initial Calibration: Five points at 5, 10, 20, 50, and 100 total nanograms.
- c) Continuing Calibration: 20 total nanograms.
- d) Surrogate Standards: SOW standards spiked as 20 ppb for base-neutral standards.
- e) Matrix Spike/Matrix Spike Duplicate: Matrix spike compounds as per the SOW spiked at 20 ppb for base-neutrals.

PESTICIDES ANALYSIS

- a) Extraction/Blowdown: Extract entire liter bottle, rinsing cap and bottle, and add to sample. Final blowdown volume may be decreased up to one-half the SOW specifications to achieve required detection limits.
- b) Surrogate Standards: SOW standards spiked as 0.2 ppb (1/5 the SOW concentration).
- c) Matrix Spike/Matrix Spike Duplicate: SOW matrix spike compounds spiked at 1/5 the SOW concentration.

ANALYTICAL RESULTS REQUIRED

- a) Quantitation Limits: Organic Analysis Data Sheets, Form 1, will reflect detection limits experimentally determined and verified previously by the contractor. This will include a method detection limit study and verification spikes at the determined MDL. The verification spikes must meet all quantitative criteria (i.e., mass spectral ions/abundances, retention times).
- b) Dilutions: The contractor will request permission of the Region to dilute any sample exceeding the initial calibration range for any parameter. Diluted and undiluted sample data will be included in the results as per the SOW.

QC REQUIREMENTS

- a) Initial Calibration: SPCC criterion apply. The %RSD for the RF's for all compounds must be $\leq 35\%$. The RF's for all other (non-SPCC) compounds must be ≥ 0.05 .
- b) Continuing Calibration: SPCC criterion apply. The %D for the RF's for all compounds must be $\leq 25\%$. The RF's for all other (non-SPCC) compounds must be ≥ 0.05 .
- c) Matrix Spike/Matrix Spike Duplicates: SOW criterion apply for %R and %RFD's.
- d) Surrogates: SOW criterion apply for %R and corrective action.
- e) Blanks: SOW criterion apply.

ATTACHMENT II

TASK: Analysis of drinking water samples for four organochlorine hydrocarbons; to be analyzed using GC/EC and GC/MS.

<u>COMPOUND</u>	REQUESTED LIMIT FOR GC/EC (ug/l)	REQUESTED LIMIT FOR GC/MS (ug/l)
Hexachloronorboradiene	0.02	1.0
Octachlorocyclopentene	0.02	1.0
Heptachloronorborene	0.02	1.0
Chlordene	0.05	1.0

WATER MATRIX SAS REQUESTS

U.S. Environmental Protection Agency
CLP Sample Management Office
P. O. Box 818, Alexandria, Virginia 22313
PHONE: (703)/557-2490 or FTS/557-2490

SAS Number

SPECIAL ANALYTICAL SERVICES
Client Request

☒ x

Regional Transmittal

☐ Telephone Request

- A. EPA Region/Client: Region V WW Engineering & Science
- B. RSCC Representative: Jan Pels
- C. Telephone Number: 312/ 353-2720
- D. Date of Request: _____
- E. Site Name: Skinner Landfill - West Chester, Ohio

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. General description of analytical service requested: _____
Analysis of water samples for chlordene, heptachloronorborene, octachlorocyclopentene,
and hexachloronorboradiene by CLP SOW 8/87 methods.
Standards may be difficult to obtain (check with EPA Pesticides Repository).
2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium, or high concentration):
Analysis of 39 low level ground water (potentially medium for VOA's) and
48 surface water samples.
Whole aqueous samples are assumed. Includes duplicates and spikes.
3. Purpose of analysis (specify whether Superfund (Remedial or Enforcement), RCRA, NPDES, etc.):
Superfund - Remedial Action

4. Estimated date(s) of collection: _____
5. Estimated date(s) and method of shipment: Daily by overnight carrier.
6. Number of days analysis and data required after laboratory receipt of samples:
Laboratory should report results within 30 days after receipt of samples.
7. Analytical protocol required (attach copy if other than a protocol currently used in this program):

CLP SOW for Organic Analysis (Multi-Media, Multi-Concentration) 8/87. Analyze
using GC/ECP according to SOW for pesticides. For samples that are greater than
requested GC/MS detection limits, analyze according to SOW for BW fraction.

8. Special technical instruction (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):

Conduct a method detection limit study prior to analysis as per 40 CFR 136,
Appendix B. Analyze as per SOW and perform required calibrations and QA/QC
using chlordene, octachlorocyclopentene, heptachlorohorborene, and hexachloro-
norboradiene.

9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.). If not completed, format of results will be left to program discretion.

As per CLP Organics SOW 8/87

10. Other (use additional sheets or attach supplementary information, as needed):

11. Name of sampling/shipping contact: Bob Phillips

Phone: 616/ 942-9600 EXT 263

I. DATA REQUIREMENTS

<u>Parameter:</u>	<u>Detection Limit</u>	<u>Precision Desired</u> <u>(+ % or Conc.)</u>
<u>Hexachloronorboradiene</u>	<u>see Table I</u>	<u>+ 20%</u>
<u>Chlordene</u>	<u>see Table I</u>	<u>+ 20%</u>
<u>Heptachloronorborene</u>	<u>see Table I</u>	<u>+ 20%</u>
<u>Octachlorocyclopentene</u>	<u>see Table I</u>	<u>+ 20%</u>
<u> </u>	<u> </u>	<u> </u>
<u> </u>	<u> </u>	<u> </u>

II. QC REQUIREMENTS

<u>Audits Required</u>	<u>Frequency of Audits</u>	<u>Limits* (% or Conc.)</u>
<u>Hexachloronorboradiene</u>	<u>see Table II</u>	<u>+ 20%</u>
<u>Chlordene</u>	<u>see Table II</u>	<u>+ 20%</u>
<u>Heptachloronorborene</u>	<u>see Table II</u>	<u>+ 20%</u>
<u>Octachlorocyclopentene</u>	<u>see Table II</u>	<u>+ 20%</u>
<u> </u>	<u> </u>	<u> </u>
<u> </u>	<u> </u>	<u> </u>
<u> </u>	<u> </u>	<u> </u>

III. ACTION REQUIRED IF LIMITS ARE EXCEEDED:

Rerun samples.

Contact: Jan Pels 312/ 353-2720 or Chuck Elly 312/ 353-9087

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for special analytical services. Should you have any questions or need any assistance, please call the Sample Management Office.

TABLE I

TASK: Analysis of water samples for four organochlorine hydrocarbons; to be analyzed using GC/EC and GC/MS.

<u>COMPOUND</u>	REQUESTED LIMIT FOR GC/EC (ug/l)	REQUESTED LIMIT FOR GC/MS (ug/l)
Hexachloronorboradiene	0.05	10
Octachlorocyclopentene	0.05	10
Heptachloronorbornene	0.05	10
Chlordane	0.05	10

TABLE II

QC LEVEL OF EFFORT FOR CLP ANALYTICAL SERVICES

<u>Method of Analysis</u>	<u>Lab Blanks</u>	<u>Spikes or Surrogates/Spikes</u>	<u>Lab Duplicates</u>	<u>Matrix Spike Duplicate</u>
GC/MS	One per set of samples or a minimum of 1 in 10	Surrogates added to each sample and matrix spikes added to one sample per set	NR	One per set of samples or a minimum of 1 in 10
GC/EC	One per set of samples or a minimum of 1 in 10	One spike per set of samples or a minimum of 1 in 10	One per set of samples or a minimum of 10	One per set of samples or a minimum of 1 in 10

5/005 -0-7/87

Chloride in Water 7/30/87

U.S. Environmental Protection Agency
CLP Sample Management Office
Box 818, Alexandria, Virginia 22313
PHONE: (703)/557-2490 or FTS/557-2490

SAS Number

SPECIAL ANALYTICAL SERVICES
Client Request

Approved For Scheduling

☒ Regional Transmittal

☐ Telephone Request

- A. EPA Region/Client: Region V WW Engineering & Science
- B. RSCC Representative: Jan Pels
- C. Telephone Number: (312) 353-2720
- D. Date of Request: _____
- E. Site Name: Skinner Landfill - West Chester, Ohio

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. General description of analytical service requested: Analysis of chloride in
water (surface waters, groundwater, drinking water, leachate, etc.). Samples will be
unfiltered. This SAS is meant for routine monitoring of waters at a waste site.
2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium, or high concentration): 39 low (potentially medium for VOA's)
ground water, 48 low surface water, 24 low drinking water samples, and
3 leachate samples.
Whole aqueous samples are assumed. Includes duplicates and blanks.
Purpose of analysis (specify whether Superfund (Remedial or Enforcement), RCRA, NPDES, etc.):
Superfund - Remedial Action

4. Estimated date(s) of collection: _____
5. Estimated date(s) and method of shipment: Daily by overnight carrier.
6. Number of days analysis and data required after laboratory receipt of samples:
Laboratory should report results within 30 days.
7. Analytical protocol required (attach copy if other than a protocol currently used in this program):
1. EPA Method 325.1 (Colorimetric, Automated Ferricyanide, AA-I) 1983ed., or
 2. EPA Method 325.2 (Colorimetric, Automated Ferricyanide, AA-II) 1983ed., or
Note: A Region V CRL Auto Analyzer Manifold is attached for Method 325.2 to correct errors in Method 325.2's manifold diagram.
 3. ASTM Colorimetric Method (Manual Method) -ASTM D 512C-81, or
 4. Method 407C (Potentiometric Titration) Standard Methods, 16th ed. Samples will be kept at 4°C until analysis and validation of results.
8. Special technical instruction (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):
- For colorimetric methods (1) use a standard curve between 0 and 300 mg/l or less, (2) the calibration curve must include 5 points or more (including a zero concentration standard), and (3) samples with absorbances or peak heights greater than highest standard must be diluted and reanalyzed. For titrimetric method 1) use either 0.0141 or 0.025 N titrant, 2) automated potentiometric titrators acceptable, 3) do not use more than 20 ml titrant for 50 ml or 100 ml sample aliquots, dilute and reanalyze any sample aliquots requiring more than 20 ml titrant, 5) remove any interfering chromate, ferric iron, sulfide, and sulfite, and 6) standardize titrants daily. Obtain approval of CPMS, CRL prior to use of any other method.
9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.). If not completed, format of results will be left to program discretion.
- The test procedure used will be clearly identified. For the colorimetric methods, bench records tabulating order of calibration standards, verification and control standards, samples, matrix spikes, titrant blanks, etc. with resulting peak height, concentration, or absorbance read-outs will be provided with copies of worksheets used to calculate results. For the titration method, any potentiometric titration curves and all bench records tabulating titrant standardization, samples, aliquot volumes, matrix spikes, etc. will be provided. Records of titrant standardization and titrant blanks will be provided. A photocopy of instrument readouts, i.e. strip charts, printer tapes, etc. must be included for all analyses. All records of analysis and calculations must be legible and sufficient to recalculate all sample concentrations and QA audit results. EPA QC reference samples, or any other reference sample or initial calibration verification, will be identified as to source, lot number, and sample number. Corresponding "true" or target values and associated 95% confidence limits for analysis results will be provided for all reference samples used.
10. Other (use additional sheets or attach supplementary information, as needed): _____
11. Name of sampling/shipping contact: Bob Phillips
- Phone: 616/ 942-9600 EXT 263

3.

DATA REQUIREMENTS

<u>Parameter:</u>	<u>Detection Limit</u>	<u>Precision Desired</u> (+% or Conc.)
<u>Chloride</u>	<u>5 mg/l</u>	<u>Differences in</u> <u>duplicate sample</u> <u>results are to be</u> <u><5 mg/l for concentrations</u> <u><50 mg/l and are to be</u> <u>< 10% for concentrations</u> <u>exceeding 50 mg/l. The</u> <u>significant figures to</u> <u>report depend on sen-</u> <u>sitivity of colorimetric</u> <u>curve or number of signifi-</u> <u>cant figures in titrant</u> <u>volume.</u>
<u>Note: These are minimum requirements</u> <u>Report actual detection limit used,</u> <u>based on allowable methodology options.</u>		

II. QC REQUIREMENTS - Do not use designated field blanks for QA Audits.

<u>Audits Required</u>	<u>Frequency of Audits</u>	<u>Limits* (% or Conc.)</u>
a) For Methods 325.1, 325.2, and ASTM D 512C		
<u>Matrix Spike*</u>	<u>1 per group of 10 or</u> <u>fewer samples</u>	<u>85 - 115% Recovery</u>
<u>Lab Duplicate</u>	<u>"</u>	<u>+ (10% or 5 mg/l)</u>
<u>Lab Blank</u>	<u>"</u>	<u><5 mg/l</u>
<u>Calibration Verification Std.</u>	<u>"</u>	<u>90-110% Recovery</u>
<u>1 Set of EPA QC Mineral Ref.</u>	<u>1 per sample set</u>	<u>85-115% Recovery</u>
<u>Samples - 2 Concentrates</u>		
b) For Method 407C		
<u>Same as Item Iia for Matrix Spike*, Lab Duplicate, and QC Mineral Reference Samples.</u>	<u>Beginning and end of</u> <u>sample set</u>	<u>-3 to +3 mg/l</u>
<u>Lab Blank (Not Titration Blank)</u>	<u>At end of sample set</u>	<u>95 - 105% Recovery</u>
<u>Calibration verification</u>		
<u>Standard (Same as Titrant Standardization)</u>		

*Matrix spike concentrations will be greater than 30% of the sample concentration, but spiked sample shall not exceed the working range of the standard curve or titration.

II. ACTION REQUIRED IF LIMITS ARE EXCEEDED:

Take corrective action and reanalyze samples - Contact Jan Pels (312) 353-2720
or Charles T. Elly (312) 353-9087.

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for special analytical services. Should you have any questions or need any assistance, please call the Sample Management Office.

5/011_-0-7/87

Sulfate in Water July 30, 1987

U.S. Environmental Protection Agency
CLP Sample Management Office
P. O. Box 818, Alexandria, Virginia 22313
PHONE: (703)/557-2490 or FTS/557-2490

SAS Number

SPECIAL ANALYTICAL SERVICES
Client Request

Approved For Scheduling

☒

Regional Transmittal

☐

Telephone Request

A. EPA Region/Client: Region V WW Engineering & Science
B. RSCC Representative: Jan Pels
C. Telephone Number: (312) 353-2720
D. Date of Request: _____
E. Site Name: Skinner Landfill - West Chester, Ohio

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. General description of analytical service requested: Analysis for sulfate in water
(surface water, groundwater, drinking water, leachate, etc.). Samples will be unfiltered.
Results are reported as mg/l SO₄.
2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium, or high concentration):
39 low (potentially medium for VOA's) groundwater; 48 low surface
water; 24 low drinking water; and 3 medium hazard leachate samples.
Whole aqueous samples assumed. Includes duplicates and blanks.
3. Purpose of analysis (specify whether Superfund (Remedial or Enforcement), RCRA, NPDES, etc.):
Superfund - Remedial Action

4. Estimated date(s) of collection: _____
Estimated date(s) and method of shipment: Daily by overnight carrier.
6. Number of days analysis and data required after laboratory receipt of samples:
Laboratory should report results within 30 days.
7. Analytical protocol required (attach copy if other than a protocol currently used in this program):
1. EPA Method 375.2 (Colorimetric Methylthmol Blue) - 1983 ed.
- Note: This method requires 0.75 mg/l SO₄ in Dilution Water(See Reagent Section 6.8)
2. Method 426C of Standard Methods, 16th ed. (Turbidimetric)
- Note: this last method provides for measurement of sulfate using 2 standard curves- 1 for sulfate concentrations between 0 and 10mg/l, and 1 between 10 and 40 mg/l sulfate.
- Samples will be kept at 4°C until validation of results.
8. Special technical instruction (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):
Sample holding time is not to exceed 28 days from date of sample collection. Sulfate standards will be prepared daily from stock solution. Samples with absorbances or turbidities greater than that in the highest standard will be diluted and rerun. For Method 426C, 1) the reanalysis solution should contain between 20 and 40 mg/l sulfate, and 2) concentrations must be corrected for background turbidity and color per Section 5d of Method 426C using pH adjusted sample aliquots. Use only the methods specified. Calibration curves must include at least 6 points (including a zero concentration standard) for Method 375.2 and Buffer A of Method 426C.
9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.). If not completed, format of results will be left to program discretion.
The test procedure used must be clearly identified. Results shall be reported as mg/l SO₄. Bench records tabulating the order of calibration standards, lab control standards, lab blanks, samples, spikes, etc., with resulting absorbances or concentration readouts, will be provided along with copies of worksheets used to calculate results. Background absorbances used for turbidity corrections must be tabulated for each sample aliquot tested. A photocopy of the instrument readout (ie. strip charts, printer tapes, etc.) must be included. All records of analysis must be legible and sufficient to calculate all concentrations and results. EPA QC reference samples, or any other reference sample or initial calibration verification, will be identified as to source, lot number, and sample number. Corresponding "true" or target values and associated 95% confidence limits for analysis results will be provided for all reference samples used.
10. Other (use additional sheets or attach supplementary information, as needed):

Name of sampling/shipping contact: Bob Phillips

Phone: 616/ 942-9600 EXT 263

I. DATA REQUIREMENTS

<u>Parameter:</u>	<u>Detection Limit</u>	<u>Precision Desired</u> (+% or Conc.)
<u>Sulfate</u>	<u>5 mg/l</u>	<u>Method 375.2:</u> Differences in duplicate sample results are to be < 5 mg/l for concentrations < 50 mg/l, and < 10% for concentrations > 50 mg/l.
		<u>Method 426 C:</u> Differences in duplicate sample results are to be < 2 mg/l for concentrations < 20 mg/l and < 10% for concentrations > 20 mg/l in aliquot tested.
<u>Note: These are minimum requirements. Report the actual detection limits used based on allowable methodology options.</u>		

II. QC REQUIREMENTS - Do not use designated field blanks for QA audits.

<u>Audits Required</u>	<u>Frequency of Audits</u>	<u>Limits* (% or Conc.)</u>
<u>Matrix Spike*</u>	<u>1 per group of 10 or fewer samples</u>	<u>85-115%</u>
<u>Lab Duplicate</u>		<u>+ (10% or 5 mg/l) for Method 375.2</u> <u>+ (10% or 2 mg/l) for Method 426C</u>
<u>Lab Blank (0 mg/l SO₄)</u>		<u>< 5 mg/l - Method 375.2</u> <u>-2 to +2mg/l-Buffer B of Method 426C or</u>
<u>Lab Blank (10 mg/l SO₄)</u>		<u>8 to 10mg/l - Buffer A of Method 426C</u>
<u>Calibration Verification Standard</u>	<u>1 per group of 10 samples and at end of sample set</u>	<u>90 - 110%</u>
<u>1 Set of EPA QC Mineral Reference Samples</u>	<u>once per sample set</u>	<u>85-115% for each concentration.</u>

*Matrix spike concentrations will be greater than 30% of sample concentrations, but spiked samples shall not exceed working range of standard curve.

III. ACTION REQUIRED IF LIMITS ARE EXCEEDED:

Take corrective action and reanalyze samples.

Contact Jan Pels (312) 353-2720 or Chuck Elly (312) 353-9087.

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for special analytical services. Should you have any questions or need any assistance, please call the Sample Management Office.

5/014__-0-6/87

Nitrate/nitrite 6/29/87

U.S. Environmental Protection Agency
CLP Sample Management Office
P. O. Box 818, Alexandria, Virginia 22313
PHONE: (703)/557-2490 or FTS/557-2490

SAS Number

APPROVED FOR SCHEDULING

SPECIAL ANALYTICAL SERVICES
Client Request

☒

Regional Transmittal

☐

Telephone Request

A. EPA Region/Client: Region V WW Engineering & Science
B. RSCC Representative: Jan Pels
C. Telephone Number: 312/ 353-2720
D. Date of Request: _____
E. Site Name: Skinner Landfill - West Chester, Ohio

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. General description of analytical service requested: Analysis of nitrate plus nitrite
(as mg/l N) in water (surface water ground water, drinking water, leachates, etc.)
Samples will be unfiltered.

2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium, or high concentration):

39 low ground water (potentially medium hazard for VOA's);
24 low drinking water; 48 low surface water; and three (3) medium hazard leachate.
Whole aqueous samples assumed. Numbers include duplicates and blanks.

3. Purpose of analysis (specify whether Superfund (Remedial or Enforcement), RCRA, NPDES, etc.):

Superfund - Remedial Action

4. Estimated date(s) of collection: _____
5. Estimated date(s) and method of shipment: Daily by overnight carrier.
6. Number of days analysis and data required after laboratory receipt of samples:
Laboratory should report results within 30 days.
7. Analytical protocol required (attach copy if other than a protocol currently used in this program):
1) EPA Method 353.1 (colorimetric, automated hydrazine reduction).
2) EPA Method 353.2 (colorimetric, automated cadmium reduction).
3) EPA Method 353.3 (colorimetric, manual cadmium reduction).
For all methods:
Samples will be stored at 4°C until analysis and validation of results. Samples will be preserved in the field with sulfuric acid (1 ml/l) to pH<2. The analytical working range shall not exceed 0.1 to 10.0 mg/l N.

For Methods 353.2 or 353.3: If more than one reduction column is used separate calibrations, QA audits, and records are required for each column. The column used must be identified for each analytical result.
8. Special technical instruction (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):
Analyze the samples within 28 days after collection. Check the sample pH (wide range pH paper is acceptable). If the pH>2 contact CPMS, CRL for instructions. Use only the methods specified in item 7. Obtain approval of CPMS, CRL before using any other method.
For Methods 353.2 and 353.3: After checking the pH it is recommended that the laboratory check for residual chlorine (or oxidizing reagents) and sulfide using test strips such as starch iodide and lead acetate papers. Contact CPMS, CRL if these interferences are present; however, the laboratory must remove these interferences prior to analysis. The laboratory must also minimize interferences due to metals in order to prolong color life. (See Section 7.1.2 of method 353.3) It is suggested that the laboratory may dilute samples up to ten-fold prior to analysis (Section 7.4 of Method 353.3) provided that the final analytical working range does not exceed 0.1 to 10.0 mg/l N.
For all methods: Neutralize samples to pH 5-9 (or to phenolphthalein color end-point) prior to analysis. Dilute and reanalyze the neutralized samples if the concentrations exceed that of the highest standard. Use at least five calibration standards (including a zero standard). Prepare the lab blank using 1 ml of H₂SO₄/l. Neutralize and analyze it like a sample.
9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.). If not completed, format of results will be left to program discretion:
The test procedure used must be clearly identified. Bench records tabulating the order of calibration standards, lab control standards, lab blanks, samples, spikes, duplicates, etc., with resulting absorbances or concentration readouts will be provided. Worksheets used to calculate results will be included. Any sample treatment to remove interferences will be documented. The laboratory shall submit photocopies of the instrument readout (strip-charts, printer tapes, etc.) All records of analysis and calculations must be legible and sufficient to recalculate all concentrations. Results are to be reported as mg N/l.
EPA QC reference samples, or any other reference sample or initial calibration verification, will be identified as to source, lot number, and sample number. Corresponding "true" or target values and associated 95% confidence limits for analysis results will be provided for all reference samples used.
10. Other (use additional sheets or attach supplementary information, as needed): _____
11. Name of sampling/shipping contact: Bob Phillips
Phone: 616/ 942-9600 EXT 263

I. DATA REQUIREMENTS

<u>Parameter:</u>	<u>Detection Limit</u>	<u>Precision Desired</u> (+/- % or Conc.)
<u>Nitrate + Nitrite</u>	<u>0.10 mg/l as N</u>	<u>Duplicate results must be within 10% for concentrations >1mg/l or within 0.1 mg/l for concentrations < 1mg/l</u>
<u>Note: These are minimum requirements. Report actual detection limits used based on allowable methodology options.</u>		<u>Results will be reported to the nearest 0.1 mg/l for conc. less than 1.0 mg/l and to 2 significant figures for conc. exceeding 1 mg/l-N.</u>

II. QC REQUIREMENTS - Do not use any designated field blanks for QA audits.

<u>Audits Required</u>	<u>Frequency of Audits</u>	<u>Limits* (% or Conc.)</u>
<u>Matrix Spike*</u>	<u>1 per group of 10 or fewer samples</u>	<u>85% - 115%</u>
<u>Lab Duplicate</u>	<u>1 per group of 10 or fewer samples</u>	<u>±(10% - or 0.10 mg/l)</u>
<u>Lab Blank (1ml/l H₂SO₄)</u>	<u>2 per sample set</u>	<u><0.1 mg/l</u>
<u>Calibration verification standard</u>	<u>1 per group of 10 or fewer samples and at end of run</u>	<u>90% - 110%</u>
<u>Calibration blank</u>	<u>1 per group of 10 samples or less</u>	<u>< 0.1 mg/l</u>
<u>1 set of EPA Nutrient QC reference samples-conc. 1 and 2, or EPA F/NO₃ QC sample, WS series Conc. 1 and 2</u>	<u>1 per sample set</u>	<u>85% - 115%</u>

*Matrix spike concentrations will be 30% or larger, of sample concentrations, but spiked samples should not exceed working concentration range of standard curve.

III. ACTION REQUIRED IF LIMITS ARE EXCEEDED:

Take corrective action and reanalyze samples. Contact Jan Pels (312) 353-2720 or Chuck Elly (312) 353-9087.

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for special analytical services. Should you have any questions or need any assistance, please call the Sample Management Office.

5/010 -0-0/0/

Ammonia in water 6/30/87

U.S. Environmental Protection Agency
CLP Sample Management Office
P. O. Box 818, Alexandria, Virginia 22313
PHONE: (703)/557-2490 or FTS/557-2490

SAS Number

SPECIAL ANALYTICAL SERVICES
Client Request

Approved For Scheduling

☒ Regional Transmittal ☐ Telephone Request

A. EPA Region/Client: Region V WW Engineering & Science
B. RSCC Representative: Jan Pels
C. Telephone Number: 312/ 353-2720
D. Date of Request: _____
E. Site Name: Skinner Landfill - West Chester, Ohio

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

- General description of analytical service requested: Analysis of ammonia
in waters (surface water, ground water, and leachate. All samples will be
unfiltered. Results will be reported as mg/l N.
- Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium, or high concentration):
48 low surface water analyses, 39 low ground water analyses, and 3 medium hazard
leachate analyses.
Whole aqueous samples assumed.
Includes duplicates and spikes,
- Purpose of analysis (specify whether Superfund (Remedial or Enforcement), RCRA, NPDES, etc.):
Superfund - Remedial Action

4. Estimated date(s) of collection: _____
5. Estimated date(s) and method of shipment: Daily by overnight carrier
6. Number of days analysis and data required after laboratory receipt of samples:
Laboratory should report results within 30 days.
7. Analytical protocol required (attach copy if other than a protocol currently used in this program):
- 1) EPA Method 350.1 (Automated Phenate), or
- 2) EPA Method 350.3 (Potentiometric, Ion Selective Electrode).
- Samples will be stored at 4° C until analysis and validation of results. Sample aliquots will be preserved in the field with sulfuric acid (1 ml/l to pH < 2).
- The working concentration range of Method 350.1 Auto Analyzer should be 0.1 to 10 mg/l NH₃-N or lesser concentration.
8. Special technical instruction (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):
- Check sample pH (wide range pH paper). If pH > 2 contact Jay Thakkar, CPMS, CRL for instructions. Dilute and rerun samples with peak heights or concentrations higher than the highest standard. The holding time is not to exceed 28 days from sample collection. All solutions should be made with ammonia-free water. For Method 350.3 calibrate the electrometer with standards in order of increasing concentration of ammonia. The pH of the solution after the addition of NaOH must be above 11. Use only the method(s) specified above. Standard curve for Method 350.1 must include at least 5 standards (one of which is zero concentration). Standard curve for Method 350.3 must include at least 4 standards between 0.1 and 10.0 mg/l NH₃-N. All standards, blanks, dilution water, and diluted samples must be acidified with 1 ml/l H₂SO₄.
9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.). If not completed, format of results will be left to program discretion:
- The test procedure used will be clearly identified. Bench records tabulating the order of calibration standards, lab blanks, samples, lab control standards, spikes, duplicate, etc. with resulting peak heights, millivolts, or concentration readouts, will be provided along with copies of worksheets used to calculate ammonia results. If Method 350.3 is used, the standard curve should be provided. A photocopy of the instrument readout i.e. strip charts, printer tapes, etc. must be included. All records analyses and calculation must be legible and sufficient to recalculate all concentrations. Results are to be in mg/-N per liter. EPA QC reference samples, or any other reference sample or initial calibration verification, will be identified as to source, lot number, and sample number. Corresponding "true" or target values and associated 95% confidence limits for analysis results will be provided for all reference samples used.
10. Other (use additional sheets or attach supplementary information, as needed):
1. Name of sampling/shipping contact: Bob Phillips
- Phone: 616/ 942-9600 EXT 263

I. DATA REQUIREMENTS

<u>Parameter:</u>	<u>Detection Limit</u>	<u>Precision Desired (+/- % or Conc.)</u>
<u>Ammonia</u>	<u>0.1 mg/l-N</u>	<u>Duplicate results must agree to within 10% for concentrations > 1mg/l or to within 0.1mg/l for concentrations < 1 mg/l</u>
<u>NOTE: These are minimum requirements. Report actual detection limits used based on specified methodologies.</u>		<u>Results will be reported to the nearest 0.05 mg/l and to 2 significant figures for concentrations exceeding 1/mg/l-N.</u>

GENERAL STATEMENT

II. QC REQUIREMENTS - Do not use designated field blanks for QA Audits.

<u>a) For Method 350.1 Audits Required</u>	<u>Frequency of Audits</u>	<u>Limits* (% or Conc.)</u>
<u>Matrix Spike*</u>	<u>at least 1 per group of 10 or fewer samples</u>	<u>85% - 115%</u>
<u>Lab Duplicate</u>	<u>at least 1 per group of 10 or fewer samples</u>	<u>+ 10% or 0.1 mg/l</u>
<u>Lab Blank</u>	<u>at least 1 per group of 10 or fewer samples</u>	<u><0.1 mg/l</u>
<u>Calibration verification</u>	<u>1 per group of 10 samples</u>	<u>90% - 110%</u>
<u>1 set of EPA QC Nutrient reference samples. Conc. 1 & 2</u>	<u>1 per sample set</u>	<u>85% - 115%</u>
<u>b) For Method 350.3</u>		
<u>Lab Duplicate</u>	<u>at least 1 per group of 10 or fewer samples</u>	<u>10% or 0.1 mg/l</u>
<u>Lab Blank</u>	<u>at least 1 per group of 10 or fewer samples</u>	<u>< 0.1 mg/l</u>
<u>Calibration verification standard</u>	<u>1 per 10 samples and end of set</u>	<u>90% - 110%</u>
<u>1 set of EPA QC Nutrient reference samples. Conc. 1 & 2</u>	<u>1 per sample set</u>	<u>85% - 115%</u>

*Matrix spike concentrations will be greater than 30% of sample concentrations, but spiked samples should not exceed working concentration range of standard curve.

III. ACTION REQUIRED IF LIMITS ARE EXCEEDED:

Take corrective action and reanalyze samples - Contact Jan Pels (312) 353-2720 or Chuck Elly (312) 353-9087.

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for special analytical services. Should you have any questions or need any assistance, please call the Sample Management Office.

5/003 -0-6/87

Alk/Acid/pH 6/29/87

U.S. Environmental Protection Agency
CLP Sample Management Office
P. O. Box 818, Alexandria, Virginia 22313
PHONE: (703)/557-2490 or FTS/557-2490

SAS Number

SPECIAL ANALYTICAL SERVICES
Client Request

Approved For Scheduling

☒

Regional Transmittal



Telephone Request

A. EPA Region/Client: Region V WW Engineering & Science
B. RSCC Representative: Jan Pels
C. Telephone Number: 312/ 353-2720
D. Date of Request: _____
E. Site Name: Skinner Landfill - West Chester, Ohio

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

- General description of analytical service requested: Analysis for alkalinity, acidity
(if necessary), and pH in waters (surface waters, groundwaters, drinking waters, leach-
ates, etc.). Samples will be unfiltered. Determine alkalinity and pH first. Only those
samples with pH values less than or equal to 5.0 or alkalinity values less than or equal
to 20 mg/l CaCO₃ will be tested for acidity. Use attached SAS for acidity (titration
after hydrogen peroxide addition and boiling), if any such determinations are required.
Report alkalinity and acidity as mg/l CaCO₃.
- Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium, or high concentration): 39 low (potentially medium for VOA's)
ground water; 24 low drinking water samples, and 3 medium hazard
leachate samples 48 low surface water samples. Whole aqueous samples assumed. Includes
duplicates and blanks.
- Purpose of analysis (specify whether Superfund (Remedial or Enforcement), RCRA, NPDES, etc.): Superfund - Remedial Action

- 2 -

4. Estimated date(s) of collection: _____
5. Estimated date(s) and method of shipment: Daily by overnight carrier.
6. Number of days analysis and data required after laboratory receipt of samples:
Laboratory should report results within 30 days of receipt of samples.
7. Analytical protocol required (attach copy if other than a protocol currently used in this program):
1) Alkalinity EPA Method 310.1 (Titrimetric, pH 4.5) or Standard Methods, 16th Edition, Method 403 4c and 4d.
2) pH - EPA Method 150.1 (Electrometric) - Initial pH of alkalinity titration is an acceptable procedure so long as sample has not been diluted.
3) Acidity - EPA Method 305.1 (Titrimetric) - Use attached SAS, and its specifications, for acidity. Determine acidity if sample pH \leq 5.0 or alkalinity \leq 20 mg/l CaCO_3 . Samples will be stored at 4°C until analysis and validation of results.
8. Special technical instruction (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):
Sample holding time should not exceed 14 days from date of collection. Use potentiometric titration to pH 4.5 for alkalinity $>$ 20 mg/l CaCO_3 . For concentrations $<$ 20 mg/l, use EPA Method 310.1 (Section 6.3) or Standard Methods, Method 403 4d. Do not use titrant volumes greater than 50 ml. Use only the Methods specified above.
Use Na_2CO_3 to standardize titrant. Standardize the pH meter and the titrant each day. Standardize the pH meter using at least two buffers which bracket the alkalinity end point. Record pH of each sample prior to titration.
9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.). If not completed, format of results will be left to program discretion.
The test procedure used will be clearly identified. Bench records tabulating the order of analysis including pH meter calibration, titrant standardization, sample pH values, lab blanks, samples, lab control standards, duplicates, etc., with resulting titrant volumes or read-outs, will be provided along with calculation worksheets. All records will be legible and sufficient to recalculate all sample concentrations and QA audit results. Report method of titrant standardization.
EPA QC reference samples, or any other reference sample, will be identified as to source, lot number, and sample number. Corresponding "true" or target values and associated 95% confidence limits for analysis results will be provided for all reference samples used.
10. Other (use additional sheets or attach supplementary information, as needed):

11. Name of sampling/shipping contact: Bob Phillips
Phone: 616/ 942-9600 EXT 263

DATA REQUIREMENTS

<u>Parameter:</u>	<u>Detection Limit</u>	<u>Precision Desired</u> (+/- or Conc.)
<u>Alkalinity (as mg/l CaCO₃)</u>	<u>2 mg/l for low level</u>	<u>+ 2 mg/l for concentrations</u> <u>< 20 mg/l CaCO₃</u>
<u>_____</u>	<u>20 mg/l for high level</u>	<u>+ 10% for concentrations</u> <u>> 20 mg/l CaCO₃</u>
<u>_____</u>	<u>_____</u>	<u>_____</u>
<u>pH</u>	<u>not applicable</u>	<u>Report to nearest</u> <u>0.1 pH values.</u>

II. QC REQUIREMENTS Do not use any field blanks for QA audits.

<u>Audits Required (Alkalinity)</u>	<u>Frequency of Audits</u>	<u>Limits* (% or Conc.)</u>
<u>lab blank</u>	<u>at least 1 per group</u> <u>of 10 or fewer samples</u>	<u>< 10 mg/l for high-level</u> <u>samples tested.</u> <u>< 2 mg/l for low-level</u> <u>samples tested.</u>
<u>lab duplicate</u>	<u>at least 1 per group</u> <u>of 10 or fewer samples</u>	<u>+ 10% or + 2 mg/l</u>
<u>lab control sample</u> <u>1 set of EPA QC mineral</u> <u>reference samples</u>	<u>1 per sample set</u>	<u>90 - 110% recovery</u>

III. ACTION REQUIRED IF LIMITS ARE EXCEEDED:

Take corrective action and reanalyze samples. Contact Jan Pels (312) 353-2720
or Chuck Elly (312) 353-9087

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for special analytical services. Should you have any questions or need any assistance, please call the Sample Management Office.

5/017 -0-7/87

BOD in Water and Wastewater 7/30/87

U.S. Environmental Protection Agency
CLP Sample Management Office
P. O. Box 818, Alexandria, Virginia 22313
PHONE: (703)/557-2490 or FTS/557-2490

SAS Number

SPECIAL ANALYTICAL SERVICES
Client Request

Approved for Scheduling

☒

Regional Transmittal

☐

Telephone Request

- A. EPA Region/Client: Region V WW Engineering & Science
- B. RSCC Representative: Jan Pels
- C. Telephone Number: (312) 353-2720
- D. Date of Request: _____
- E. Site Name: Skinner Landfill - West Chester, Ohio

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. General description of analytical service requested: Analysis of
biological oxygen demand (BOD) in water and leachate. Samples will be unfiltered.
Results are reported as mg/l oxygen.
2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium, or high concentration):
39 low ground water (potentially medium hazard for VOA's) and 3 medium
hazard leachate samples.
Whole aqueous samples assumed. Includes duplicates and blanks.
3. Purpose of analysis (specify whether Superfund (Remedial or Enforcement), RCRA, NPDES, etc.):
Superfund - Remedial Action

5/017G-0-7/87

3.

BOD in Water and Wastewater 7/30/87

I. DATA REQUIREMENTS

<u>Parameter:</u>	<u>Detection Limit</u>	<u>Precision Desired</u> (+/- % or Conc.)
<u>BOD</u>	<u>2 mg/l</u>	<u>Differences in duplicate series of sample results shall not exceed 2 mg/l for concentrations less than 20mg/l.</u>
<u> </u>	<u> </u>	<u> </u>
<u> </u>	<u> </u>	<u> </u>

II. QC REQUIREMENTS Do not use any field blanks for QA audits.

<u>Audits Required</u>	<u>Frequency of Audits</u>	<u>Limits* (% or Conc.)</u>
<u>Glucose-Glutamic acid checks</u>	<u>1 pair per set of samples</u>	<u>160-240 mg/l</u>
<u>Duplicate (full dilution series)</u>	<u>at least 1 per group of 10 or fewer samples</u>	<u>+ or -(10% or 2 mg/l)</u>
<u>Unseeded Dilution Water Blanks</u>	<u>1 pair per set of samples, including 1 pair for each lot of dilution water</u>	<u>< or = to 0.2 mg/l</u>
<u>DO Uptake of seed in seeded dilution water (calculated)</u>	<u>calculated for each lot of seeded dilution water</u>	<u>0.6 to 1.0 mg/l</u>
<u>1 set of EPA QC Demand Reference Samples (if specified)</u> Yes <u> </u> No <u> </u>	<u>1 set of 2 per sample set</u>	<u>75 - 125% Recovery</u>

III. ACTION REQUIRED IF LIMITS ARE EXCEEDED:

Take corrective action and reanalyze samples - Contact Jan Pels (312) 353-2720
or Chuck Elly (312) 353-9087.

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for special analytical services. Should you have any questions or need any assistance, please call the Sample Management Office..

5/018__-0-6/87

COD (Hi- and Lo-levels) 6/26/87

U.S. Environmental Protection Agency
CLP Sample Management Office
P. O. Box 818, Alexandria, Virginia 22313
PHONE: (703)/557-2490 or FTS/557-2490

SAS Number

SPECIAL ANALYTICAL SERVICES
Client Request

Approved for Scheduling

☒

Regional Transmittal

☐

Telephone Request

WW Engineering & Science

A. EPA Region/Client: Region V

B. RSCC Representative: Jan Pels

C. Telephone Number: 312/353-2720

D. Date of Request: _____

E. Site Name: Skinner Landfill - West Chester, Ohio

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. General description of analytical service requested:

Analysis of chemical oxygen demand (COD) (Hi-level) (50 - 800 mg/l) and COD (Lo-level) (5 - 50 mg/l) in water (groundwater, leachate). Samples will be unfiltered. Any sample with COD values less than 50 mg/l will be determined and reported as COD (Lo-level). Samples with COD values greater than or equal to 50 mg/l will be determined and reported as COD (Hi-level). The COD (Lo-level) method is used for optimum precision and accuracy of measurement of low concentration COD values.

If field specific conductance values are greater than or equal to 5000 umhos/cm, field personnel will indicate this on the SAS Packing Lists or any future RAS/SAS Traffic Report Forms, the field conductance values and the instruction "Check for Possible Chloride Interference in COD Test" for any such samples. If this is the case or if there is other definite knowledge of chlorides exceeding 2000 mg/l, the laboratory will determine the chloride content and inhibit chloride interference pursuant to Section 7.1 of EPA Method 410.3.

NOTE: It is expected that few waters from Region V (<3%), will have chloride concentrations in excess of 2000 mg/l, however, it is the responsibility of field personnel to first identify any samples having a chloride interference for COD so that the COD test can be modified to compensate for any chloride interference.

Results are reported as mg/l COD.

2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium, or high concentration): 39 low (potentially medium for VOA's) ground water and 3 medium hazard leachate samples. Whole aqueous samples assumed. Includes duplicates and blanks.

3. Purpose of analysis (specify whether Superfund (Remedial or Enforcement), RCRA, NPDES, etc.):

Superfund - Remedial Action

4. Estimated date(s) of collection: _____
5. Estimated date(s) and method of shipment: Daily by overnight carrier.
6. Number of days analysis and data required after laboratory receipt of samples:
Laboratory should report results within 30 days.

7. Analytical protocol required (attach copy if other than a protocol currently used in this program):

EPA Method 410.1 (Titrimetric, Mid-level) for COD > 50 mg/l.

EPA Method 410.2 (Titrimetric, Low-level) for COD < 50 mg/l.

Use Section 7.1 of Method 410.3 if chloride concentration exceeds 2000 mg/l in a sample.

If titration blank is necessary for each different amount of mercuric sulfate used for inhibition of chloride interference, SAS Packing Lists will note the samples requiring assessment of chloride interferences. Measurement of chloride will be done using any method of "Standard Methods", 16th ed., or "EPA Methods for Chemical Analysis of Water and Wastes", 1983 ed., whenever possible chloride interference is noted.

Samples will be preserved with 1 ml of H₂SO₄ to pH less than 2 and kept at 4°C until sample analysis and validation of results are completed. Holding time is not to exceed 28 days from date of sample collection.

8. Special technical instruction (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):

1. Check sample pH (wide range pH paper). If pH > 2, contact CPMS, CRL for further instructions.
2. Use a) 50 ml sample aliquots for both methods, b) 0.250 N K₂Cr₂O₇ reagent and 0.25 N ferrous ammonium sulfate titrant for Method 410.1, and c) 0.0250 N K₂Cr₂O₇ reagent and 0.025 N ferrous ammonium sulfate titrant for Method 410.2.
3. Dilute and reanalyze (by Method 410.1) any samples with COD values > 800 mg/l or titrant volumes < 5.0 ml. Reanalyze samples (by Method 410.1) if initial sample values are > 50 mg/l COD by Method 410.2. Reanalyze samples (by Method 410.2) if initial sample values are < 50 mg/l COD by Method 410.1.
4. Any sample aliquots < 50 mls will be diluted to 50 mls so that the COD reaction mixture will be 50% H₂SO₄/ 50% water by volume.
5. Titration blanks will be determined, at least in duplicate each day of analysis and will not differ more than ± 0.1 ml titrant for Method 410.1 and ± 1.0 ml titrant for Method 410.2.
6. Separate sets of QA Audits will be performed for each method, if both methods are used.
7. Use potassium hydrogen phthalate as a matrix spike compound. Use 20 mg/l matrix spike concentration for Method 410.2.
8. Samples will be refluxed for at least 2 hours.
9. Homogenize sample aliquots, as necessary, to obtain sample aliquots of representative suspended solids.
10. Use only the method specified.

5/018__-0-6/87

(2)

COD (Hi- and Lo-levels)
6/26/87

9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.). If not completed, format of results will be left to program discretion.

Bench records, tabulating titrant standardization, titration volumes for titration or sample blanks (2 or more in number), samples, and QA Audits will be provided for each method used. All records of analysis and calculations must be legible and sufficient to recalculate all sample concentrations and QA Audit results. Records of chloride analysis will be provided for any samples so specified on the RAS/SAS Traffic Report or SAS Packing List. Separate bench records will be provided for any COD determinations of high chloride samples (>2000 mg/l Cl) including weight of mercuric sulfate used, sample titration volume and titration blank volume for each sample type. EPA QC Reference samples, or any other reference samples, will be identified as to source, lot number, and sample number. Corresponding "true" or target values and associated 95% confidence limits for analysis results will be provided for all reference samples used.

10. Other (use additional sheets or attach supplementary information, as needed):

11. Name of sampling/shipping contact: Bob Phillips

Phone: 616/ 942-9600 EXT 263

I. DATA REQUIREMENTS

<u>Parameter:</u>	<u>Detection Limit</u>	<u>Precision Desired</u> (+/- % or Conc.)
<u>COD (Method 410.1)</u>	<u>50 mg/l</u>	Method 410.1: Differences in sample duplicates are to be < or = to 0.2 ml titrant or < 8 mg/l for concentrations < 80 mg/l and < 10% for COD concentrations exceeding 80 mg/l. Method 410.2: Differences in sample duplicate results are to be < 1.0 ml titrant or < 4 mg/l for concentrations less than 40 mg/l and are to be < 5 mg/l for concentrations between 40 50 mg/l.
<u>COD (Method 410.2)</u>	<u>5 mg/l</u>	
<u>NOTE: These are minimum requirements. Report actual detection limits used based on specified methodologies.</u>		

II. QC REQUIREMENTS

<u>Audits Required</u>	<u>Frequency of Audits</u>	<u>Limits* (% or Conc.)</u>
<u>Matrix spike (KHP)</u>	<u>at least 1 per group of 10 or fewer samples</u>	
<u>Method 410.1*</u>		<u>85 - 115% Recovery (410.1)</u>
<u>Method 410.2(Use 20 mg/l spike)</u>		<u>75 - 125% Recovery (410.2)</u>
<u>Lab duplicate</u>	<u>" "</u>	<u>Diff ≤ (8 mg/l or 10%) (410.1)</u> <u>Diff ≤ (4 mg/l - 5 mg/l) (410.2)</u>
<u>Titration blank (used for calculation of results)</u>	<u>at least 2 per sample set for each method used</u>	<u>Diff in titrant volumes shall not exceed 0.1 ml for 410.1 and 1.0 ml for 410.2</u>
<u>1 set of EPA QC Demand Reference samples - 2 concentration levels</u>	<u>1 per sample set for each method used</u>	<u>90 - 110% Recovery or < 8 mg/l error for 410.1 and < 5 mg/l error for 410.2 in aliquot tested</u>

* - Matrix spike will be greater than 30% of the sample concentration, but spiked sample shall not exceed 800 mg/l for Method 410.1.

III. ACTION REQUIRED IF LIMITS ARE EXCEEDED:

Take corrective action and reanalyze samples. Contact Jan Pels (312) 353-2720 or Chuck Elly (312) 353-9087.

Contact Region V RSCC Jan Pels (312) 353-2720 concerning questions on chloride interferences and modifications of COD test.

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for special analytical services. Should you have any questions or need any assistance, please call the Sample Management Office.

5/015__-0-7/87

Total Kjeldahl Nitrogen in Water
July 30, 1987

U.S. Environmental Protection Agency
CLP Sample Management Office
P.O. Box 818, Alexandria, Virginia 22313
TE: (703)/557-2490 or FTS/557-2490

SAS Number

SPECIAL ANALYTICAL SERVICES
Client Request

Scheduled for Approval

☒

Regional Transmittal

☐

Telephone Request

- A. EPA Region/Client: Region V WW Engineering & Science
- B. RSCC Representative: Jan Pels
- C. Telephone Number: (312) 353-2720
- D. Date of Request: _____
- E. Site Name: Skinner Landfill - West Chester, Ohio

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. General description of analytical service requested: Analysis for total Kjeldahl
nitrogen in waters (, groundwaters, , leachates, etc.).
All samples will be unfiltered. Results will be reported as mg/l N.
2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium, or high concentration):
39 low (potentially medium for VOA's) ground water, 3 and medium hazard
leachate samples.
Whole aqueous samples assumed. Includes duplicates and blanks.
3. Purpose of analysis (specify whether Superfund (Remedial or Enforcement), RCRA, NPDES, etc.):
Superfund - Remedial Action

5/015 -0-7/87

Total Kjeldahl Nitrogen July 30, 1987

- 2 -

4. Estimated date(s) of collection: _____
5. Estimated date(s) and method of shipment: Daily by overnight carrier.
6. Number of days analysis and data required after laboratory receipt of samples:
Laboratories shall report results within 30 days after receipt of samples.
7. Analytical protocol required (attach copy if other than a protocol currently used in this program):
1) EPA Method 351.2 (Colorimetric, Block Digester, AA II)
2) EPA Method 351.3 (Colorimetric, Titrimetric, or Potentiometric) (NOTE: For Method 351.3 the micro-Kjeldahl technique is not acceptable.) Samples will be preserved in the field using H₂SO₄ (1ml/L) to pH<2, samples will be stored at 4°C until analysis and validation of results.
8. Special technical instruction (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):
For all Methods: Analyze samples within 28 days after collection. Check the sample pH (wide range pH paper). If the pH>2, contact CPMS, CRL for instructions. Use nicotinic acid for the control standard. Use an organic nitrogen compound for the matrix spike. Use only the Methods specified in item 7. Method 351.3 requires distillation separation, prior to all final ammonia measurements. For Method 351.3: Use only the Colorimetric method for samples containing less than 1 mg N/l.
For Colorimetric Methods (351.2 and 351.3): Use at least five calibration standards (including a zero concentration standard). Dilute and reanalyze samples with concentrations that exceed the highest calibration standard.
For the Potentiometric Method (351.3): Use at least four calibration standards. Dilute and reanalyze samples with concentrations that exceed the highest calibration standard.
For the Titrimetric Method (351.3): Standardize the titrant each day. Include records of indicator blank.
9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.). If not completed, format of results will be left to program discretion.
Identify the test procedure and options used. Provide bench records and all records of calibration, analyses, and calculations for standards, samples, blanks, any titration indicator blanks, duplicates, spikes, controls, etc. Include absorbances, peak heights, responses, concentrations, etc. for each measurement. Include digestion logs showing sample volumes and dilutions for all samples. Identify organic nitrogen compound used for matrix spikes. Records must be legible and sufficient to recalculate all concentrations and QA audit results. Provide photocopies of all instrument readouts (i.e. stripcharts, print-outs, etc). Report results as mg N/l. Identify the compound used for the matrix spike.
EPA QC reference samples, or any other reference sample or initial calibration verification, will be identified as to source, lot number, and sample number. Corresponding "true" or target values and associated 95% confidence limits for analysis results will be provided for all reference samples used.
10. Other (use additional sheets or attach supplementary information, as needed):

11. Name of sampling/shipping contact: Bob Phillips
Phone: 616/ 942-9600 EXT 263

3.

I. DATA REQUIREMENTS

<u>Parameter:</u>	<u>Detection Limit</u>	<u>Precision Desired</u> (+/- % or Conc.)
TKN	0.1 mg N/l	Duplicate sample results must agree within 0.1 mg/l for concentrations < 1 mg/l and within 10% for concentrations > or = to 1 mg/l
NOTE: These are minimum requirements. Report the actual detection limit used based on allowable methodology options.		

II. QC REQUIREMENTS Do not use designated field blanks for QA audits.

<u>Audits Required</u>	<u>Frequency of Audits</u>	<u>Limits* (% or Conc.)</u>
Control standards (Nicotinic Acid)	one per set	70 - 110% recovery
Matrix spike*	one per group of 10 or fewer samples	85 - 115% recovery
Lab duplicate	" "	+ (10% or 0.1 mg N/l)
Lab blank	" "	+ 0.1 mg N/l
Calibration verification Standard	" " and at the end of the set	90 - 110%
1 set of EPA QC nutrient reference samples conc. 3 and 4.	one per set	85 - 115%

*Matrix spike concentration will be greater than 30% of the sample concentration but will not exceed the highest calibration standard. Matrix spikes will be prepared from an organic nitrogen compound.

III. ACTION REQUIRED IF LIMITS ARE EXCEEDED:

Take corrective action and reanalyze samples.

Contact Chuck Elly (312) 353-9087 or Jan Pels (312) 353-2720

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for special analytical services. Should you have any questions or need any assistance, please call the Sample Management Office.

5/020 -0-6/87

Total Organic Carbon in Water 6/30/87

U.S. Environmental Protection Agency
CLP Sample Management Office
P. O. Box 818, Alexandria, Virginia 22313
PHONE: (703)/557-2490 or FTS/557-2490

SAS Number

SPECIAL ANALYTICAL SERVICES
Client Request

Approved For Scheduling

☒

Regional Transmittal

☐

Telephone Request

- A. EPA Region/Client: Region V WW Engineering & Science
- B. RSCC Representative: Jan Pels
- C. Telephone Number: (312) 353-2720
- D. Date of Request: _____
- E. Site Name: Skinner Landfill - West Chester, Ohio

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. General description of analytical service requested: Analysis for total organic carbon in water (surface waters, groundwaters, , leachate, etc.). Most samples will be unfiltered, although certain aliquots can be filtered and preserved at the time of collection. Results are reported as mg/l C.
2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium, or high concentration):
39 low (potentially medium for VOA's) ground water, 3 medium hazard leachate, and 48 low surface water samples.
Whole aqueous samples assumed. Includes duplicates and blanks.
3. Purpose of analysis (specify whether Superfund (Remedial or Enforcement), RCRA, NPDES, etc.):
Superfund - Remedial Action

4. Estimated date(s) of collection: _____
Estimated date(s) and method of shipment: Daily by overnight carrier.
6. Number of days analysis and data required after laboratory receipt of samples:
Laboratory should report results within 30 days of receipt of samples.
7. Analytical protocol required (attach copy if other than a protocol currently used in this program):
EPA Method 415.1 (combustion or oxidation).
Samples will be preserved with 1 ml/l H₂SO₄ to pH <2. Samples will be stored at 4°C until analysis and validation of results.
8. Special technical instruction (if outside protocol requirements) dilute and rerun samples with absorbances higher than the highest standard:
Check sample pH with (wide range pH paper). If pH >2 contact CPMS, CRL for instructions. The holding time is not to exceed 28 days from sample collection. Homogenize samples if necessary. Qualify results where suspended solids content may affect accuracy. Instruments with syringe injection will utilize 2 injections per measurement. If the 2 injections differ by more than 10% or 2 mg/l, repeat and report the average of 4 injections. Inorganic carbon will be purged from solution or, if determined separately, subtracted from total carbon values. Obtain approval of CPMS, CRL, prior to use of any other method. The calibration curve must include at least 5 standards. (One of the standards must be zero concentration).
9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.). If not completed, format of results will be left to program discretion:
Test procedures and specific instrument used will be clearly identified. Bench records tabulating order of calibration standards, lab blanks, samples lab control standards, spikes, duplicates etc., with resulting output on concentration readout will be provided along with worksheets used to calculate results. Specify the organic compound used to prepare standards and spikes. A photocopy of the instrument readout, i.e. stripcharts, printer, tapes, etc. must be included. Results are to be reported in mg/l C. Records of analysis and calculations must be legible and sufficient to recalculate all concentrations. EPA QC reference samples, or any other reference sample or initial calibration verification, will be identified as to source, lot number, and sample number. Corresponding "true" or target values and associated 95% confidence limits for analysis results will be provided for all reference samples used.
10. Other (use additional sheets or attach supplementary information, as needed):

Name of sampling/shipping contact: Bob Phillips

Phone: 616/ 942-9600 EXT 263

I. DATA REQUIREMENTS

<u>Parameter:</u>	<u>Detection Limit</u>	<u>Precision Desired</u> <u>(+/- % or Conc.)</u>
<u>TOC</u>	<u>2 mg/l</u>	<u>Difference in duplicate results should not exceed + 10% for concentrations >20 mg/l or 2 mg/l for concentrations less than 20 mg/l.</u>
<u>NOTE: These are minimum requirements. Report actual detection limits used based on specified methodologies.</u>		

II. QC REQUIREMENTS - Do not use designated field blanks for QA audits.

<u>Audits Required</u>	<u>Frequency of Audits</u>	<u>Limits* (% or Conc.)</u>
<u>Matrix Spike*</u>	<u>at least 1 per group of 10 or fewer samples</u>	<u>85% - 115%</u>
<u>Lab Duplicate</u>	<u>at least 1 per group of 10 or fewer samples</u>	<u>+ (10% or 2.0 mg/l)</u>
<u>Lab Blank</u>	<u>at least 1 per group of 10 or fewer samples</u>	<u>≤ 2.0 mg/l</u>
<u>Calibration verification standard</u>	<u>1 per group of 10 samples and end of set</u>	<u>90% - 110%</u>
<u>1 set of EPA demand QC reference samples (conc. 1 and 2)</u>	<u>1 per sample set</u>	<u>85% - 115%</u>

*The matrix spike concentrations will be approximately 30% of sample concentrations, but spiked samples shall not exceed the working range of the standard curve.

III. ACTION REQUIRED IF LIMITS ARE EXCEEDED:

Take corrective action and reanalyze samples - Contact Jan Pels (312) 353-2720
or Chuck Elly (312) 353-9087.

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for special analytical services. Should you have any questions or need any assistance, please call the Sample Management Office.

5/003_-0-6/87

Alk/Acid/pH 6/29/87

U.S. Environmental Protection Agency
CLP Sample Management Office
P. O. Box 818, Alexandria, Virginia 22313
PHONE: (703)/557-2490 or FTS/557-2490

SAS Number

SPECIAL ANALYTICAL SERVICES
Client Request

Approved For Scheduling

☒

Regional Transmittal

☐

Telephone Request

- A. EPA Region/Client: Region V WW Engineering & Science
- B. RSCC Representative: Jan Pels
- C. Telephone Number: 312/ 353-2720
- D. Date of Request: _____
- E. Site Name: Skinner Landfill - West Chester, Ohio

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. General description of analytical service requested: Analysis for alkalinity, acidity
(if necessary), and pH in waters (. groundwaters, surface waters
). Samples will be unfiltered. Determine alkalinity and pH first. Only those
samples with pH values less than or equal to 5.0 or alkalinity values less than or equal
to 20 mg/l CaCO₃ will be tested for acidity. Use attached SAS for acidity (titration
after hydrogen peroxide addition and boiling), if any such determinations are required.
Report alkalinity and acidity as mg/l CaCO₃.
2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium, or high concentration): 39 low (potentially medium for
VOA's) ground water, 48 low surface water, 3 medium hazard leachate, and
24 low drinking water samples. Whole aqueous samples assumed. Includes duplicates
and blanks.
3. Purpose of analysis (specify whether Superfund (Remedial or Enforcement), RCRA, NPDES, etc.): Superfund - Remedial Action

- 2 -

4. Estimated date(s) of collection: _____
5. Estimated date(s) and method of shipment: Daily by overnight carrier.
6. Number of days analysis and data required after laboratory receipt of samples:
Laboratory should report results within 30 days of receipt of samples.
7. Analytical protocol required (attach copy if other than a protocol currently used in this program):
1) Alkalinity EPA Method 310.1 (Titrimetric, pH 4.5) or Standard Methods, 16th Edition, Method 403 4c and 4d.
2) pH - EPA Method 150.1 (Electrometric) - Initial pH of alkalinity titration is an acceptable procedure so long as sample has not been diluted.
3) Acidity - EPA Method 305.1 (Titrimetric) - Use attached SAS, and its specifications, for acidity. Determine acidity if sample pH \leq 5.0 or alkalinity \leq 20 mg/l CaCO_3 . Samples will be stored at 4°C until analysis and validation of results.
8. Special technical instruction (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):
Sample holding time should not exceed 14 days from date of collection. Use potentiometric titration to pH 4.5 for alkalinity $>$ 20 mg/l CaCO_3 . For concentrations $<$ 20 mg/l, use EPA Method 310.1 (Section 6.3) or Standard Methods, Method 403 4d. Do not use titrant volumes greater than 50 ml. Use only the Methods specified above.
Use Na_2CO_3 to standardize titrant. Standardize the pH meter and the titrant each day. Standardize the pH meter using at least two buffers which bracket the alkalinity end point. Record pH of each sample prior to titration.
9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.). If not completed, format of results will be left to program discretion.
The test procedure used will be clearly identified. Bench records tabulating the order of analysis including pH meter calibration, titrant standardization, sample pH values, lab blanks, samples, lab control standards, duplicates, etc., with resulting titrant volumes or read-outs, will be provided along with calculation worksheets. All records will be legible and sufficient to recalculate all sample concentrations and QA audit results. Report method of titrant standardization.
EPA QC reference samples, or any other reference sample, will be identified as to source, lot number, and sample number. Corresponding "true" or target values and associated 95% confidence limits for analysis results will be provided for all reference samples used.
10. Other (use additional sheets or attach supplementary information, as needed):

11. Name of sampling/shipping contact: Bob Phillips
Phone: 616/ 942-9600 EXT 263

DATA REQUIREMENTS

<u>Parameter:</u>	<u>Detection Limit</u>	<u>Precision Desired</u> <u>(+ % or Conc.)</u>
<u>Alkalinity (as mg/l CaCO₃)</u>	<u>2 mg/l for low level</u>	<u>+ 2 mg/l for concentrations</u> <u>< 20 mg/l CaCO₃</u>
<u>_____</u>	<u>20 mg/l for high level</u>	<u>+ 10% for concentrations</u> <u>> 20 mg/l CaCO₃</u>
<u>pH</u>	<u>not applicable</u>	<u>Report to nearest</u> <u>0.1 pH values.</u>

II. QC REQUIREMENTS Do not use any field blanks for QA audits.

<u>Audits Required (Alkalinity)</u>	<u>Frequency of Audits</u>	<u>Limits* (% or Conc.)</u>
<u>lab blank</u>	<u>at least 1 per group</u> <u>of 10 or fewer samples</u>	<u>< 10 mg/l for high-level</u> <u>samples tested.</u> <u>≤ 2 mg/l for low-level</u> <u>samples tested.</u>
<u>lab duplicate</u>	<u>at least 1 per group</u> <u>of 10 or fewer samples</u>	<u>+ 10% or + 2 mg/l</u>
<u>lab control sample</u> <u>1 set of EPA QC mineral</u> <u>reference samples</u>	<u>1 per sample set</u>	<u>90 - 110% recovery</u>

III. ACTION REQUIRED IF LIMITS ARE EXCEEDED:

Take corrective action and reanalyze samples. Contact Jan Pels (312) 353-2720
or Chuck Elly (312) 353-9087

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for special analytical services. Should you have any questions or need any assistance, please call the Sample Management Office.

5/016__-0-6/87

Total Phosphorus in H₂O 6/29/87

U.S. Environmental Protection Agency
CLP Sample Management Office
P. O. Box 818, Alexandria, Virginia 22313
PHONE: (703)/557-2490 or FTS/557-2490

SAS Number

SPECIAL ANALYTICAL SERVICES
Client Request

Approved For Scheduling

☒

Regional Transmittal

☐

Telephone Request

- A. EPA Region/Client: Region V WW Engineering & Science
- B. RSCC Representative: Jan Pels
- C. Telephone Number: (312) 353-2720
- D. Date of Request: _____
- E. Site Name: Skinner Landfill - West Chester, Ohio

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. General description of analytical service requested: Analysis for total phosphorous
in waters (surface waters, ground waters, leachate, etc.). Most samples
will be unfiltered although certain aliquots can be filtered and preserved at time of
collection. Results will be reported as mg/l P. Ground water samples will be filtered.
2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium, or high concentration):
39 low (potentially medium for VOA's) ground water; 48 low surface
water; and 3 medium hazardous leachate water samples. Whole aqueous samples assumed.
Includes duplicates and blanks.
3. Purpose of analysis (specify whether Superfund (Remedial or Enforcement), RCRA, NPDES, etc.):
Superfund - Remedial Action

4. Estimated date(s) of collection: _____
5. Estimated date(s) and method of shipment: Daily by overnight carrier.
- Number of days analysis and data required after laboratory receipt of samples:
Laboratory should report results within 30 days after receipt of samples.
7. Analytical protocol required (attach copy if other than a protocol currently used in this program):
Total Phosphorus EPA Method 365.1 (Automated, Colorimetric, Ascorbic Acid)
Total Phosphorus EPA Method 365.2 (Automated, Colorimetric, Single Reagent)
Total Phosphorus EPA Method 365.4 (Block Digestor)
Samples will be preserved in the field with 1 ml/l H₂SO₄ to pH <2 and stored at 4°C until analysis and validation of results.
8. Special technical instruction (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.) Check sample pH using wide-range pH paper. If the pH>2, contact CPMS, CRL for instructions:
Dilute and redigest samples with absorbances or peak heights higher than the highest standard. All standards, blanks, audits, etc. must be digested. The holding time is not to exceed 28 days from sample collection. Use only the method(s) specified above. The calibration curve must include at least 5 standards. (One of the standards must be zero concentration).
9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.). If not completed, format of results will be left to program discretion:
The test procedure used will be clearly identified. Bench records and all records of analysis and calculations for samples, blanks, duplicates, spikes and all control checks with peak height or response and concentrations will be provided with copies of worksheets. Results will be reported as mg/l P. Any digestion log will be provided showing sample aliquots and concentrations of all samples tested. Records must be legible and sufficient to recalculate all concentrations. A photocopy of the instrument readout i.e. stripcharts, printer tapes, etc. must be included. EPA QC reference samples, or any other reference sample or initial calibration verification, will be identified as to source, lot number, and sample number. Corresponding "true" or target values and associated 95% confidence limits for analysis results will be provided for all reference samples used.
10. Other (use additional sheets or attach supplementary information, as needed):

11. Name of sampling/shipping contact: Bob Phillips
Phone: 616/ 942-9600 EXT 263

I. DATA REQUIREMENTS

<u>Parameter:</u>	<u>Detection Limit</u>	<u>Precision Desired</u> (<u>±%</u> or Conc.)
<u>Total P</u>	<u>0.05 mg/l</u>	<u>Duplicate results must agree to within 10% for concentrations > 0.5 mg/l or within 0.05 mg/l for concentrations < 0.5 mg/l</u>
<u>NOTE: These are minimum requirements. Report actual detection limits used based on specified methodologies.</u>		

II. QC REQUIREMENTS - Do not use designated field blanks for QA audits

<u>Audits Required</u>	<u>Frequency of Audits</u>	<u>Limits* (% or Conc.)</u>
<u>Matrix Spike*</u>	<u>at least 1 per group of 10 or fewer samples</u>	<u>85% - 115%</u>
<u>Lab Duplicate</u>	<u>at least 1 per group of 10 or fewer samples</u>	<u>± (10% or 0.05 mg/l)</u>
<u>Lab Blank (Also serves as a calibration blank).</u>	<u>at least 1 per group of 10 or fewer samples</u>	<u><0.05 mg/l</u>
<u>Calibration verification standard</u>	<u>1 per group of 10 samples and end of sample set</u>	<u>90% - 110%</u>
<u>1 set of EPA nutrient QC reference samples conc. 3&4</u>	<u>1 per sample set</u>	<u>85% - 115%</u>

*The matrix spike concentrations will be approximately 30% or larger of sample concentrations, but spiked samples shall not exceed the working range of the standard curve.

III. ACTION REQUIRED IF LIMITS ARE EXCEEDED:

Take corrective action and reanalyze samples.

Contact Jan Pels (312) 353-2720 or Chuck Eilly (312) 353-9087.

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for special analytical services. Should you have any questions or need any assistance, please call the Sample Management Office.

5/024 -0-6/87

Total Dissolved Solids 6/29/87

U.S. Environmental Protection Agency
HWI Sample Management Office
P.O. Box 818, Alexandria, Virginia 22313
Phone: (703) 557-2490 or FTS-557-2490

SAS Number

Special Analytical Services
Regional Request

☒ Regional Transmittal

☐ Telephone Request

A. EPA Region and Site Name: Region V WW Engineering & Science
B. Regional Representative: Jan Pels
C. Telephone Number: (312) 353-2720
D. Data request: _____
E. Site Name: Skinner Landfill - West Chester, Ohio

Please provide below a description of your request for Special Analytical Services under the Uncontrolled Hazardous Waste Dumpsite Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. General description of analytical service requested: Analysis of total dissolved solids (180°C) in water (surface waters, etc.) Results are reported as mg/l dissolved solids.

2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium, or high concentration):

48 low surface water analyses.

Whole aqueous samples assumed.

Includes duplicates and blanks.

3. Purpose of analysis (specify whether Superfund (Remedial or Enforcement), RCRA, NPDES, etc.):

Superfund - Remedial Action

4. Estimated date(s) of collection: _____

5. Estimated date(s) and method of shipment: Daily by overnight carrier.

6. Approximate number of days results required after lab receipt of samples: _____

Laboratory should report results within 30 days.

7. Analytical protocol required (attach copy if other than a protocol currently used in this program):

1. EPA Method 160.1, 1983 ed., or

2. Method 209B, "Standard Methods", 16th ed. Samples will be kept at 4°C until

sample analysis and validation of results. Holding time is 7 days from date of sample collection.

8. Special technical instructions (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):

1) Use standard aliquots of 100ml; however do not use sample aliquots yielding more than 200 mg residue. If residue is greater than 200 mg, repeat the analysis using a smaller sample aliquot. 2) If the pH value is less than 4.0, raise the pH of the aliquot (using NaOH titrant) to between pH 4 and 8 and subtract the weight of sodium added from the weight of the residue.

3) Residue will be weighed either to constant weight pursuant to Section 7.6 of Method 160.1 the final weight is to be used for calculations. Constant weight is defined as a) less than 0.5 mg or less than 4% weight loss from the previous weight, whichever is smaller, or b) dried overnight (12 hours drying time) with a single weight used for calculations.

9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.). If not completed, format of results will be left to program discretion.

Identify the QC reference sample lot numbers used and their true values with 95% confidence intervals. Bench records of tare weights, final weights, additional weights to determine constant weights, volumes filtered, blanks, duplicate samples, and reference samples will be provided with copies of work sheets used to calculate results. Dates and time of 1) determination of tare weights, 2) sample filtration, and 3) determination of residue weights and constant residue weights will be part of bench records. All records of analysis must be legible and sufficient to recalculate all sample concentrations and QA results.

10. Other (use additional sheets or attach supplementary information, as needed):

11. Name of sampling/shipping contact: Bob Phillips

Phone: 616/ 942-9600 EXT 263

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for special analytical services. Should you have any question or need any assistance, please call the Sample Management Office.

I. DATA REQUIREMENTS

<u>Parameter</u>	<u>Detection Limit</u>	<u>Precision Desired</u> (+/- % or Conc.)
TDS	20 mg/l	Difference in duplicate sample aliquots shall not exceed 2 mg for residues. Duplicate differences shall not exceed 10% for sample values greater than 200 mg/l.
Note: These are minimum requirements. Report the actual detection limits used based on allowable methodology options.		

II. QUALITY CONTROL REQUIREMENTS Do not use any designated field blanks for QA Audits.

<u>Audits Required</u>	<u>Frequency of Audits</u>	<u>Limits* (+/- % or Conc.)</u>
1. 1 set of EPA QC Mineral Reference Samples*- 2 concentration levels.	1 per sample set	85-115% Recovery
2. Lab Duplicate	At least 1 per group of 10 or fewer samples	+/- (10% or 2 mg of residue)
3. Lab Blanks (100 ml of filtered reagent water)	At least 1 per group of 10 or fewer samples	- 20 mg/l to + 20 mg/l

* Alternate reference samples must be approved by Region V RSCC prior to analysis.

III. *Action Required if Limits are Exceeded:

Take corrective action and retest samples. Contact Charles T. Elly (312/353-9087) or

Jan Pels (312/ 353-2720)

5/025 -0-6/87

Total suspended solids in water 6/29/87

U.S. Environmental Protection Agency
HWI Sample Management Office
P.O. Box 818, Alexandria, Virginia 22313
Phone: (703) 557-2490 or FTS-557-2490

SAS Number

Special Analytical Services
Regional Request

Approved for Scheduling

☒

Regional Transmittal

☐

Telephone Request

A. EPA Region and Site Name: Region V WW Engineering & Science
B. Regional Representative: Jan Pels
C. Telephone Number: () 312/ 393-2720
D. Data request:
E. Site Name: Skinner Landfill - West Chester, Ohio

Please provide below a description of your request for Special Analytical Services under the Uncontrolled Hazardous Waste Dumpsite Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. General description of analytical service requested: Analysis for total suspended solids (103-105°C) in water (surface waters, etc.) Results are reported as mg/l total suspended solids.

2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium, or high concentration):

48 low surface water analyses.

Whole aqueous samples assumed.

Includes duplicates and blanks.

3. Purpose of analysis (specify whether Superfund (Remedial or Enforcement), RCRA, NPDES, etc.):

Superfund Remedial Action

4. Estimated date(s) of collection:

5. Estimated date(s) and method of shipment: Daily by overnight carrier.

6. Approximate number of days results required after lab receipt of samples: _____
Laboratory should report results within 30 days.
7. Analytical protocol required (attach copy if other than a protocol currently used in this program):
1. EPA Method 160.2, 1983 ed., (Gravimetric, Dried at 103° - 105° C) using glass fiber filter discs without organic binder such as: Millipore AP-40, Reeve Angel 934-AH, Gelman A/E, or equivalent. Use only membrane filter apparatus with 47 mm diameter glass fiber filter and a coarse (40-60 micron) fritted disc filter support. The filter and support specifications are mandatory. Samples will be held at 4°C until sample analysis and validation of results are completed. Holding time is 7 days from date of sample collection.
8. Special technical instructions (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):
1. Sample aliquot volumes are selected on the basis of the following factors. a) During initial sample filtration, filtration rate should not drop rapidly, or require more than 5 minutes of filtration time. (Increase the filter area or decrease the sample volume as needed for sample reanalysis), b) The sample aliquot filtered should provide a residue with greater than 1.0 mg for aliquots less than 200ml in volume, and c) Sample aliquots should not exceed 200ml in volume. 2. Duplicate sample aliquots will be filtered with 2 or more intervening samples. 3. Final residues are to be weighed either to constant weight pursuant to Section 7.6 of Method 160.1 (The final weight is to be used for calculations), or dried overnight (12 hours of drying time) with the single weight used for calculations. Constant weight is defined as less than 0.5 mg or less than 4% weight loss from the previous weight, whichever is smaller. 4. Use only the method specified above in items 7 and 8.
9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.). If not completed, format of results will be left to program discretion.
- Identify EPA QC reference sample lot numbers used and their true values and 95% confidence intervals. Bench records of tare weights, final weights, volumes filtered, blanks, duplicate samples, and reference samples (all in the order filtered) will be provided along with copies of worksheets used to calculate results. Dates and time of a) filtration of initial 100ml volume, b) determination of tare weights, c) sample filtration, and d) determination of constant residue weights will be part of bench records. All records of analysis must be legible and sufficient to recalculate all sample concentrations and QA results.
10. Other (use additional sheets or attach supplementary information, as needed):

11. Name of sampling/shipping contact: Bob Phillips
Phone: 616/ 942-9600 EXT 263

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for special analytical services. Should you have any questions or need any assistance, please call the Sample Management Office.

I. DATA REQUIREMENTS

<u>Parameter</u>	<u>Detection Limit</u>	<u>Precision Desired</u> (+/- or Conc.)
<u>Suspended Solids</u>	<u>2-3 mg/l for 200 ml</u>	<u>Difference in duplicate</u>
<u>Note: These are minimum</u>	<u>sample aliquot</u>	<u>results shall not exceed</u>
<u>requirements. Report the</u>		<u>0.5 mg for duplicate</u>
<u>actual detection limits</u>		<u>aliquots filtered.</u>
<u>used based on allowable</u>		
<u>methodology options.</u>		

II. QUALITY CONTROL REQUIREMENTS Do not use designated field blanks for QA Audits.

<u>Audits Required</u>	<u>Frequency of Audits</u>	<u>Limits* (+/- or Conc.)</u>
<u>1) Lab Duplicates</u>	<u>1 per group of 10 or</u>	<u>less than 0.5 mg</u>
<u>(See item 8.3 on Page 2)</u>	<u>fewer samples</u>	
<u>2) Lab Blanks</u>	<u>1 per group of 10 or</u>	<u>-0.5 to +0.5 mg</u>
<u>(200 ml aliquots)</u>	<u>fewer samples</u>	
<u>3) 1 set of 2 EPA QC</u>	<u>1 per sample set</u>	<u>< 5 mg/l error for con-</u>
<u>Residue Reference</u>		<u>centrations < to 50 mg/l</u>
<u>Samples-2 concentration</u>		<u>or < or = to 10% for nom-</u>
<u>levels</u>		<u>inal concentrations > than</u>
		<u>50 mg/l</u>

* Alternate reference samples must be approved by Region V RSCC prior to analysis.

III. *Action Required if Limits are Exceeded:

Take corrective action and reanalyze samples.

Contact Jan Pels (312) 353-2720 or Chuck Elly (312) 353-9087.

SOLID MATRIX SAS REQUESTS

U.S. Environmental Protection Agency
CLP Sample Management Office
P. O. Box 818, Alexandria, Virginia 22313
PHONE: (703)/557-2490 or FTS/557-2490

SAS Number

SPECIAL ANALYTICAL SERVICES
Client Request

☒

Regional Transmittal

☐

Telephone Request

- A. EPA Region/Client: Region V WW Engineering & Science
- B. RSCC Representative: Jan Pels
- C. Telephone Number: 312/ 353-2720
- D. Date of Request: _____
- E. Site Name: Skinner Landfill - West Chester, Ohio

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. General description of analytical service requested: High hazard waste sample analysis for chlordene, heptachloronorborene, hexachloronorboradiene, and octachlorocyclopentene using SAS 3900-1 protocol. Analysis by GC/MS using B/N fraction method. Standards may be difficult to obtain. Contact EPA Pesticide Repository.
2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium, or high concentration):
58 high hazard waste samples.
Whole solid samples assumed.
Includes duplicates and spikes.
3. Purpose of analysis (specify whether Superfund (Remedial or Enforcement), RCRA, NPDES, etc.):
Superfund - Remedial Action

4. Estimated date(s) of collection: _____
5. Estimated date(s) and method of shipment: Daily by overnight carrier.
6. Number of days analysis and data required after laboratory receipt of samples:
Laboratory should report results within 30 days.
7. Analytical protocol required (attach copy if other than a protocol currently used in this program):
SAS 3900-I (high concentration organic support). Use B/N method for analysis of
chlordene, octachlorocyclopentene, heptachloronorborene, and hexachloronorboradiene.

8. Special technical instruction (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):
Perform method detection limit study as per 40 CFR 136 Appendix B. Conduct all
calibrations and QA/QC data using chlordene, octachlorocyclopentene, heptachloro-
norborene, and hexachloronorboradiene.

9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.). If not completed, format of results will be left to program discretion.
As per SAS 3900-I.

10. Other (use additional sheets or attach supplementary information, as needed):

11. Name of sampling/shipping contact: Bob Phillips
Phone: 616/942-9600 EXT 263

I. DATA REQUIREMENTS

<u>Parameter:</u>	<u>Detection Limit</u>	<u>Precision Desired</u> <u>(+/- % or Conc.)</u>
<u>Chlordene</u>	<u>20 mg/kg</u>	<u>+ 35%</u>
<u>Hexachloronorboradiene</u>	<u>20 mg/kg</u>	<u>+ 35%</u>
<u>Heptachloronorbornene</u>	<u>20 mg/kg</u>	<u>+ 35%</u>
<u>Octachlorocyclopentene</u>	<u>20 mg/kg</u>	<u>+ 35%</u>
<u> </u>	<u> </u>	<u> </u>
<u> </u>	<u> </u>	<u> </u>

II. QC REQUIREMENTS

[illegible]

III. ACTION REQUIRED IF LIMITS ARE EXCEEDED:

As per SAS 3900-I.

Contact: Jan Pels 312/ 353-2720 or Chuck Elly 312/ 353-9087

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for special analytical services. Should you have any questions or need any assistance, please call the Sample Management Office.

U.S. Environmental Protection Agency
CLP Sample Management Office
P. O. Box 818, Alexandria, Virginia 22313
PHONE: (703)/557-2490 or FTS/557-2490

SAS Number

SPECIAL ANALYTICAL SERVICES
Client Request

☒

Regional Transmittal



Telephone Request

- A. EPA Region/Client: Region V WW Engineering & Science
- B. RSCC Representative: Jan Pels
- C. Telephone Number: 312/ 353-2720
- D. Date of Request: _____
- E. Site Name: Skinner Landfill - West Chester, Ohio

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. General description of analytical service requested: _____
Analysis of soil and sediment samples for chlordene, heptachloronorborene,
octachlorocyclopentene, and hexachloronorboradiene by CLP SOW 8/87 methods.
Standards may be difficult to obtain (check with EPA Pesticide Repository).
2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium, or high concentration):
80 low level soil and 48 low level sediment samples.
Whole solid samples assumed. Includes duplicates and spikes.
Purpose of analysis (specify whether Superfund (Remedial or Enforcement), RCRA, NPDES, etc.):
Superfund - Remedial Action

4. Estimated date(s) of collection: _____
5. Estimated date(s) and method of shipment: Daily by overnight carrier.
6. Number of days analysis and data required after laboratory receipt of samples:
Laboratory should report results within 30 days after receipt of samples.
7. Analytical protocol required (attach copy if other than a protocol currently used in this program):
CLP SOW for Organic Analysis (Multi-Media, Multi-Concentration) 8/87. Analyze
using GC/ECP according to SOW for pesticides. For samples that are greater than
requested GC/MS detection limits, analyze according to SOW for BW fraction.
8. Special technical instruction (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):
Conduct a method detection limit study prior to analysis as per 40 CFR 136,
Appendix B. Analyze as per SOW and perform required calibrations and QA/QC
using chlordene, octachlorocyclopentene, heptachloroboroborene, and hexachloro-
norboradiene.
9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.). If not completed, format of results will be left to program discretion.
As per CLP Organics SOW 8/87
10. Other (use additional sheets or attach supplementary information, as needed):
11. Name of sampling/shipping contact: Bob Phillips
Phone: 616/ 942-9600 EXT 263

I. DATA REQUIREMENTS

<u>Parameter:</u>	<u>Detection Limit</u>	<u>Precision Desired</u> (<u>±</u> % or Conc.)
Hexachloronorboradiene	see Table I	<u>±</u> 20%
Chlordene	see Table I	<u>±</u> 20%
Heptachloronorborene	see Table I	<u>±</u> 20%
Octachlorocyclopentene	see Table I	<u>±</u> 20%

II. QC REQUIREMENTS

<u>Audits Required</u>	<u>Frequency of Audits</u>	<u>Limits* (% or Conc.)</u>
<u>Hexachloronorboradiene</u>	<u>see Table II</u>	<u>+ 20%</u>
<u>Chlordene</u>	<u>see Table II</u>	<u>+ 20%</u>
<u>Heptachloronorborene</u>	<u>see Table II</u>	<u>+ 20%</u>
<u>Octachlorocyclopentene</u>	<u>see Table II</u>	<u>+ 20%</u>
<u> </u>	<u> </u>	<u> </u>
<u> </u>	<u> </u>	<u> </u>

III. ACTION REQUIRED IF LIMITS ARE EXCEEDED:

Rerun samples.

Contact: Jan Pels 312/ 353-2720 or Chuck Elly 312/ 353-9087

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for special analytical services. Should you have any questions or need any assistance, please call the Sample Management Office.

TABLE I

TASK: Analysis of soil samples for four organochlorine hydrocarbons; to be analyzed using GC/EC and GC/MS.

<u>COMPOUND</u>	REQUESTED LIMIT FOR GC/EC (ug/g)	REQUESTED LIMIT FOR GC/MS (ug/g)
Hexachloronorboradiene	0.05	10
Octachlorocyclopentene	0.05	10
Heptachloronorborene	0.05	10
Chlordene	0.05	10

TABLE II

QC LEVEL OF EFFORT FOR CLP ANALYTICAL SERVICES

<u>Method of Analysis</u>	<u>Lab Blanks</u>	<u>Spikes or Surrogates/Spikes</u>	<u>Lab Duplicates</u>	<u>Matrix Spike Duplicate</u>
GC/MS	One per set of samples or a minimum of 1 in 10	Surrogates added to each sample and matrix spikes added to one sample per set	NR	One per set of samples or a minimum of 1 in 10
GC/EC	One per set of samples or a minimum of 1 in 10	One spike per set of samples or a minimum of 1 in 10	One per set of samples or a minimum of 10	One per set of samples or a minimum of 1 in 10

U.S. Environmental Protection Agency
CLP Sample Management Office
P. O. Box 818, Alexandria, Virginia 22313
PHONE: (703)/557-2490 or FTS/557-2490

SAS Number

SPECIAL ANALYTICAL SERVICES
Client Request

☒

Regional Transmittal

☐

Telephone Request

- A. EPA Region/Client: EPA Region V WW Engineering & Science
- B. RSCC Representative: Jan Pels
- C. Telephone Number: 312/ 353-2720
- D. Date of Request: _____
- E. Site Name: Skinner Landfill - West Chester, Ohio

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. General description of analytical service requested: 2, 3, 7, 8 specific tetra-
chlorinated dibenzodioxin and dibenzofuran, total tetra through octa polychlorinated
dibenzodioxins and dibenzofurans, and percent moisture.

2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium, or high concentration):

Analysis of 58 high hazard waste samples containing low levels of dioxins and
furans.

Includes duplicates and blanks.

3. Purpose of analysis (specify whether Superfund (Remedial or Enforcement), RCRA, NPDES, etc.):

Superfund - Remedial Action

4. Estimated date(s) of collection: _____
5. Estimated date(s) and method of shipment: Daily by overnight carrier.
6. Number of days analysis and data required after laboratory receipt of samples:
Laboratory should report results within 45 days.
7. Analytical protocol required (attach copy if other than a protocol currently used in this program):
Extraction: Benzene soxhlet as described in Anal. Chem, 1980, 52, 2045-2054 (Appendix I). Clean-up: HPLC/RPHPLC as described in above reference or Dioxin IFB
WA-86K357 options including carbon column cleanup as needed to meet surrogate percent recovery limits (Appendix II). Instrument: Use HRMS or LRMS to meet target
detection limits.
8. Special technical instruction (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):
1) Determine and report percent moisture (use CLP IFB protocol - Appendix III).
2) Report all data on dry weight basis.
3) Stir soil samples for 30 seconds before removing aliquot.
4) Quantitation and standards requirements (Appendix IV).
5) MUST monitor for the masses of the polychlorinated diphenyl ether interferences
in all furan isomer groups.
9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.): If not completed, format of results will be left to program discretion.
Appendix V for deliverables.
Appendix VI for suggested data report format.
Remember to report percent moisture.
10. Other (use additional sheets or attach supplementary information, as needed):
DO NOT SUBCONTRACT WITHOUT PRIOR REGIONAL APPROVAL.
11. Name of sampling/shipping contact: Bob Phillips
Phone: 616/ 942-9600 EXT 263

I. DATA REQUIREMENTS

<u>Parameter:</u>	<u>Detection Limit</u>	<u>Precision Desired</u> <u>(+/- % or Conc.)</u>
<u>2378 - TCDD/TCDF</u>	<u>5 ppt</u>	<u> </u>
<u>Total TCDD/TCDF</u>	<u>5 ppt</u>	<u> </u>
<u>Total Penta CDD/CDF</u>	<u>20 ppt</u>	<u> </u>
<u>Total Hexa CDD/CDF</u>	<u>20 ppt</u>	<u> </u>
<u>Total Hepta CDD/CDF</u>	<u>20 ppt</u>	<u> </u>
<u>OCDD/OCDF</u>	<u>50 ppt</u>	<u> </u>

II. QC REQUIREMENTS

<u>Audits Required</u>	<u>Frequency of Audits</u>	<u>Limits* (% or Conc.)</u>
<u>Method Blank</u>	<u>1 per 20 SPLS or set</u>	<u>less than Target D.L</u>
<u>In-Lab Matrix Spike</u>	<u> </u>	<u>see attachment</u>
<u>Matrix Spike Duplicate</u>	<u> </u>	<u>see attachment</u>
<u>Surrogate Spikes</u>	<u>in every sample</u>	<u> </u>
<u> </u>	<u> </u>	<u> </u>
<u> </u>	<u> </u>	<u> </u>
<u> </u>	<u> </u>	<u> </u>

III. ACTION REQUIRED IF LIMITS ARE EXCEEDED:

1) FOLLOW PROCEDURES SPECIFIED IN DIOXIN IFB WA-86K357 (Appendix II).

2) Call Region V if problem persists. Jan Pels 312/ 353-2720 or

Chuck Elly 312/ 353-9087

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for special analytical services. Should you have any questions or need any assistance, please call the Sample Management Office.

11. Surrogate, Duplicate and Matrix Spike Limits

A. In Laboratory Matrix Spike

Compound	Level		Recovery Limits
2378-TCDD	< 50 ppt		70 - 130%
2378-TCDF	< 50 ppt		70 - 130%
Penta CDD/CDF	< 200 ppt	*	40 - 160%
Hexa CDD/CDF	< 200 ppt	*	40 - 160%
Hepta CDD/CDF	< 200 ppt	*	40 - 160%
OCDD/OCDF	< 500 ppt	.*	40 - 160%

* At least one isomer from each of these classes should be used in the spike solution.

B. Surrogate Spikes (required in every sample)

Surrogate	Level ^a	Recovery Limits
³⁷ Cl ₄ 2378-TCDD	5 ng	50 - 115%
¹³ C ₁₂ or ³⁷ Cl ₄ 2378-TCDF ^{Pe CDD}	5 ng	50 - 115%
³⁷Cl₄ OCDD or ¹³ C ₁₂ -HxCDD	10 - 20 ng	40 - 110%

^aAdded to 10g sample

C. In Matrix Spike Duplicate

Class	RPD Limit
2378- TCDD/TCDF	< 30% RPD
Penta CDD/CDF	< 60% RPD
Hexa CDD/CDF	< 60% RPD
Hepta CDD/CDF	< 60% RPD
OCDD/OCDF	< 30% RPD

Determination of Tetra-, Hexa-, Hepta-, and Octachlorodibenzo-*p*-dioxin Isomers in Particulate Samples at Parts per Trillion Levels

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An analytical procedure is presented which permits the isomer-specific determination of tetra-, hexa-, hepta-, and octachlorodibenzo-*p*-dioxins simultaneously at parts per trillion concentrations. Typical data are presented to establish its applicability on a variety of environmental particulate samples. The use of a highly specific sample clean-up procedure based on multiple chromatographies is shown to permit the isomer-specific determination of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2378-TCDD) by packed-column gas chromatography-low-resolution mass spectrometry in the presence of any or all other TCDD isomers.

The determination of parts per trillion (10^{-12} g/g, ppt) concentrations of chemical residues generally requires the use of either highly selective sample purification procedures and/or very specific detectors (1, 2). As detection limits are lowered, the number of possible interferences present at significant concentrations increases dramatically (3). Donaldson (4) has surmised that every known organic chemical could be detected in water at a level of 10^{-12} g/g or higher. Similarly, considering an analysis at the 10 ppt concentration level in a sample matrix that is 99.9% pure, interference from as many as 10^3 compounds at concentrations 10^3 times higher than the component of interest are possible. Naturally the addition of interferences from sources other than the sample matrix can make this task formidable. Such contamination of laboratory reagents by a multitude of compounds has been reported (5-19). Indeed, in some cases, the controlling factor in determining the limit of detection (LoD) for a given analysis is not the instrumental sensitivity of the detector but the apparent response observed in reagent blanks (20-22).

This paper reports the development of an analytical procedure which permits the isomer-specific determination of 2378-TCDD at low parts per trillion concentrations, even in matrices that have been intentionally fortified with equivalent amounts of each of the other 21 TCDD isomers. Higher chlorinated dioxins, including hexachlorodibenzo-*p*-dioxins (HCDDs, 10 possible isomers), heptachlorodibenzo-*p*-dioxins (H₇CDDs, 2 possible isomers), and octachlorodibenzo-*p*-dioxin (OCDD), can also be determined at low parts per trillion levels by using this technique. In regards to the isomer-specific determination of 2378-TCDD, the other 21 TCDD isomers may also be considered as possible interferences. Several publications have recently appeared which demonstrate CDD determination capabilities but do not provide complete TCDD isomer specificity (23-32).

EXPERIMENTAL SECTION

Reagents. The preparation of 44% concentrated sulfuric acid on silica, 10% silver nitrate on silica, basic alumina, and purified nitrogen (Fentogas) have been described (1).

Silica. This adsorbent is prepared from chromatographic grade silicic acid as described for the preparation of 44% sulfuric acid on silica (1).

32% 1 M Sodium Hydroxide on Silica. The silica support is prepared as described (1). Activated silica is weighed into an appropriately sized glass bottle. On the basis of the support

weight, the amount of 1 M aqueous sodium hydroxide necessary to yield a reagent containing 32% by weight is added in a stepwise fashion with shaking to produce a uniformly coated, free-flowing powder.

Chemicals and Solvents. All solvents used are Burdick and Jackson, distilled-in-glass quality. Laboratory chemicals (H_2SO_4 , $AgNO_3$, $NaOH$) are ACS reagent grade. These materials are tested by subjecting them to the analytical procedure to verify the absence of contamination. Spectrophotometric grade Gold-label *n*-hexadecane was obtained from Aldrich Chemical Co. (Milwaukee, WI) and was purified by passage through basic alumina.

Expendables. Pyrex glass wool, silica boiling stones, and disposable pipettes are cleaned before use. Glass wool and boiling stones are Soxhlet extracted ~1 h consecutively with the following solvents: methanol, chloroform + benzene (1:1 by volume), benzene, and methylene chloride. They are then dried in a hot air oven at ~160 °C for ~1 h. Disposable pipettes are cleaned ultrasonically in deionized water and then methanol and finally methylene chloride prior to drying at ~160 °C. Final sample residues are stored in React-Vials obtained from Pierce Chemical Co. (Rockford, IL). The vials are cleaned by washing with detergent and water and then boiled sequentially in benzene + chloroform + methanol (1:1:1 by volume), benzene + chloroform (1:1 by volume), benzene, and finally methylene chloride. They are air-dried and again rinsed with methylene chloride immediately before use.

Dioxin Standards. The primary standard of 2378-TCDD was prepared by W. W. Muellder (Dow Chemical Co.) and its structure was confirmed by single-crystal X-ray diffraction techniques (33). Purity was assessed at 98% by mass spectrometry. Standards of other TCDD isomers were synthesized and isolated as previously described (34). Primary standards of 1,2,3,4,6,7,8-heptachlorodibenzo-*p*-dioxin (1234678-H₇CDD) and OCDD were synthesized by H. G. Pravel and W. W. Muellder (Dow Chemical Co.). A standard containing two HCDD isomers was prepared by Aniline (35). Standards of 1234679-H₇CDD and the 10 HCDD isomers were synthesized and isolated in a manner similar to that reported for TCDDs (34). Isotope-enriched ¹⁴C-2378-TCDD and ¹⁴C-123478-HCDD were synthesized by A. S. Kende (University of Rochester, Rochester, NY). Mass spectrometric analysis indicated these standards to be 86 atom % and 43 atom % ¹⁴C, respectively. Perchlorination of the ¹⁴C-2378-TCDD provided ¹⁴C-OCDD.

Apparatus. Reverse-Phase High-Performance Liquid Chromatography (RP-HPLC). Residues containing chlorinated dioxins are injected into the RP-HPLC system: column, two 6.2 x 250 mm Zorbax-ODS (DuPont Instruments Division, Wilmington, DE) columns in series; isocratic eluent, methanol at 2.0 mL/min; pump, Altex Model 110A; column temperature, 50 °C; UV detector, Perkin-Elmer Model LC-65T liquid chromatographic column oven and detector operated at 0.02 au at 235 nm; injector, Rheodyne Model 7120 with 50-μL sample loop.

Normal-Phase Adsorption High-Performance Liquid Chromatography (Silica-HPLC). Residues containing TCDDs are injected into the silica-HPLC system: column, two 6.2 x 250 mm Zorbax-SIL (DuPont Instruments Division) columns in series; isocratic eluent, hexane at 2.0 mL/min; pump, Altex Model 110A; column temperature, ambient; UV detector, Laboratory Data Control Model 1204 variable-wavelength detector at 0.05 au at 235 nm; injector, Rheodyne Model 7120 with 100-μL sample injection loop. The columns were activated by the procedure of Bredeweg et al. (36).

Packed-Column Gas Chromatography-Low-Resolution Mass Spectrometry (GC-LRMS). Chlorinated dioxin quantification

was accomplished by GC-LRMS using a Hewlett-Packard Model 5992-A operating in the selected ion mode (SIM) at unit resolution: column, 2 mm i.d. \times 210 cm silylated glass; packing, 0.60% OV-17 silicone + 0.40% Poly S-179 on 80/100 mesh Permabond Methyl Silicone-10 cycle (HNU Systems Inc., Newton, MA); injection port temperature, 230 °C on-column; carrier gas, helium at 14 cm³/min; separator, single stage glass jet operating at column temperature; electron energy, 70 eV. TCDD analyses conditions: column temperature, 248 °C isothermal; ions monitored, native TCDDs at *m/e* 320, 322, and 324, and ¹⁴C-2378-TCDD internal standard at *m/e* 332. Higher chlorinated dioxin analyses conditions: column temperature, programmed from 230 to 300 °C at 10 °C/min and hold at maximum; ions monitored, native HCDDs at *m/e* 388, 390, and 392, native H₂CDDs at *m/e* 422, 424, and 426, and native OCDD at *m/e* 468, 460, and 462. ¹⁴C-123478-HCDD and ¹⁴C-OCDD are monitored at *m/e* 396 and 470, respectively.

Environmental Particulate Samples. Industrial Dust. Particulates were removed from the air intake filtration system from a research building located in Midland, MI.

Electrostatically Precipitated Fly Ash. Particulates were collected from the ash-removal system associated with the electrostatic precipitator on the Nashville Thermal Transfer Corp. refuse incinerator located in Nashville, TN.

Activated Municipal Sludge. Representative samples were removed from the center of a commercially purchased 20-kg bag of Milwaukee Micropurite.

Urban Particulate Matter. Standard Reference Material No. 1648 was obtained from the National Bureau of Standards (NBS).

European Fly Ash. Particulate emissions from a municipal trash incinerator were collected on filter paper by a nonisokinetic sampling procedure. The location of the sampling port was downstream from the electrostatic precipitator. This incinerator was not operated to recover energy for power generation.

Sample Preparation. Prior to GC-LRMS SIM quantification, the sample is prepared by using five basic steps: (1) chlorinated dioxins removal from the matrix via hydrocarbon extraction, (2) chemically modified adsorbent treatment of the extract to remove easily oxidizable species, (3) adsorbent treatment to remove common chemical interferences, (4) RP-HPLC residue fractionation to remove residual chemically similar interferences and to separate dioxins present into groups according to their degree of chlorination, and (5) silica-HPLC refractionation of the RP-HPLC TCDD fractions to provide a second high-efficiency chromatographic separation having different selectivity to remove residual interferences and to permit TCDD isomer specificity.

An appropriately sized all-glass Soxhlet extraction apparatus equipped with a water-cooled condenser, a 43 \times 125 mm glass thimble with coarse frit, a 250-mL boiling flask, and a temperature-controlled heating mantle is assembled. Each of the parts is thoroughly scrubbed with an aqueous detergent solution, rinsed with deionized water followed by acetone, methanol, and methylene chloride, and finally air-dried. Depending on the particulate sample size (larger samples require most), 8–15 g of silica is charged into the thimble followed by a plug of glass wool large enough to cover the silica bed completely. The assembled system (thimble installed) is charged with benzene (~250 mL) and allowed to reflux at a recycle rate of ~20 mL/min for a minimum period of 2 h. Following this preextraction period, the system is permitted to cool and the total benzene extract is discarded. The extraction thimble is removed and allowed to drain completely on a clean wire stand in a fume hood. The glass wool plug is removed with clean forceps while a representative particulate sample, ranging from 50 mg for filtered airborne particulates to 100 g for heavy soils, is quickly charged on top of the silica bed. The glass wool plug is replaced and the thimble returned to the Soxhlet extractor body. At this time aliquots of isooctane internal standard solutions containing isotopically labeled 2378-TCDD, 123478-HCDD, and OCDD are introduced directly into the particulates bed. The system is recharged with fresh benzene and exhaustively extracted at the rate previously described for a minimum period of 16 h. Each sample or set should have at least one system treated as described for the sample to serve as a reagent blank.

Upon completion of the prescribed extraction period, the flask containing the benzene extract is removed and fitted with a three-

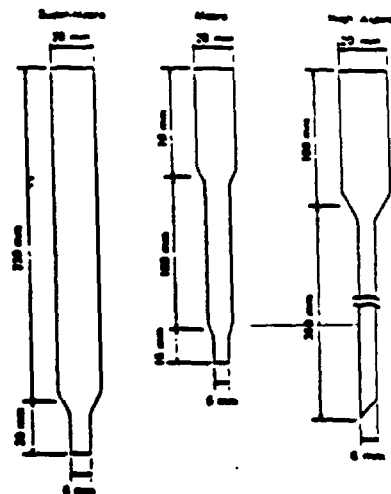


Figure 1. Liquid chromatographic clean-up columns.

to six-stage Snyder distillation column. The volume of the extract solution is then reduced by atmospheric pressure distillation of the benzene solvent to a final volume of approximately 25 mL. The concentrated benzene extract is then diluted with a roughly equal volume of hexane when cool.

Bulk matrix (benzene extractables other than CDDs) removal is accomplished by passing the residue extract solution through a Super-Macro chromatographic column (see Figure 1) prepared as follows. The column is thoroughly washed and dried just prior to use via the same procedure described for the Soxhlet extractor. A glass wool plug is inserted into the end of the column to serve as a bed support, and the following reagents are then carefully weighed directly into the column: 1.0 g of silica (bottom layer), 2.0 g of 33% 1 M sodium hydroxide on silica, 1.0 g of silica, 4.0 g of 44% concentrated sulfuric acid on silica, and 2.0 g of silica (top layer). The freshly packed column is then immediately prewashed with 30 mL of hexane and the effluent discarded. The residue extract is then passed through the column followed by 3 \times 5-mL hexane rinses of the boiling flask vessel. Following these rinses an additional 30 mL of hexane is passed through the column. The total effluent is collected in a 150-mL beaker and then evaporated to dryness under a stream of Fentogas nitrogen. A single drop of *n*-hexadecane (~25 mg) is added to the reagent blank prior to its evaporation to dryness as a means of improving internal standard recovery.

Common chemical interferences are removed by passage of the residue through a dual column system consisting of a top Macro chromatographic column draining into a bottom High Aspect column. (See Figure 1.) Each of these columns is cleaned as previously described and a glass wool bed support inserted just prior to use. The Macro column is packed with 1.5 g of 10% silver nitrate on silica and prewashed with 15 mL of hexane prior to use. The High Aspect column is packed with 5.0 g of basic alumina. When the top Macro column prewash has drained, it is positioned over the High Aspect column reservoir. The sample residue is dissolved in ~15 mL of hexane and introduced into the top column followed by 3 \times 5-mL hexane beaker rinses. Following the rinses, an additional 30 mL of hexane is passed through the system. When drained, the top column is discarded. After the hexane has drained to bed level in the High Aspect column, 50 mL of 50% (v/v) carbon tetrachloride in hexane is passed through. The total effluent to this point can be discarded. A 25-mL glass vial (cleaned same as chromatographic columns) is used to collect the total effluent after 22.5 mL of 50% (v/v) methylene chloride in hexane is introduced into the column. When elution is complete this fraction which contains chlorinated dioxins is evaporated to dryness under a stream of Fentogas nitrogen (7).

RP-HPLC fractionation of the residue is initiated by calibration of the appropriate collection zones for TCDDs, HCDDs, H₂CDDs, and OCDDs.

Table I. TCDD Isomer RP-HPLC Fractionation Scheme and Specific Retention Indices

TCDD isomer	RP-HPLC abs RT, ^a min	silica- HPLC rel RT ^b	GC packed column rel RT ^c
RP-Iso No. 1 Fraction			
1269	11.8-13.0	1.702	0.998
1469	11.6-13.0	1.497	0.912
1267/1239	12.2-12.9	1.623	1.081
	12.2-12.9	1.795	1.200
1268/1279	13.3-13.9	1.238	0.956
	13.3-13.9	1.291	1.065
1369/1478	13.3-13.9	1.220	0.802
	13.3-13.9	1.340	0.907
RP-2378 Fraction			
1246/1249	13.7-14.5	1.323	0.896
	13.7-14.5	1.411	0.898
2378	13.8-14.5	1.000	1.006 ^d
1236/1239	13.8-14.4	1.356	1.037
	14.4-15.2	1.350	0.969
1278	14.0-14.7	1.288	0.893
1237/1238	14.0-15.0	1.100	0.979
	14.0-15.0	1.128	0.990
1247/1248	14.2-15.1	1.154	0.854
	14.2-15.1	1.199	0.857
RP-Iso No. 2 Fraction			
1378	14.9-15.7	1.000	0.858
1379	14.9-15.9	0.940	0.771
1368	15.3-16.8	0.977	0.729
1234	15.8-16.8	1.248	0.960

^a RP-HPLC abs RT = absolute retention time (± 0.1 min) to collect peak. ^b Silica-HPLC rel RT = retention time relative to 2378-TCDD (± 0.010). ^c GC-packed column rel RT = retention time relative to ¹⁴C-2378-TCDD (± 0.005). ^d Native 2378-TCDD elutes slightly later than ¹⁴C-2378-TCDD.

subjected to reverse-phase high-performance liquid chromatography fractionation. The resultant liquid chromatograms monitored by a UV detector at 235 nm ($\sim \lambda_{\text{max}}$ for TCDDs) and 0.02 a.u. are shown in Figure 3b-f. Shown in Figure 3a is the chromatogram obtained for a CDD calibration standard by RP-HPLC. Although the appropriate CDD collection zones, denoted by dotted lines, were initially established by individual injections of 22 TCDD isomers, 10 HCDD isomers, 2 H-CDD isomers, and OCDD, we routinely compute their location from the observed retention times of only a few selected species. The specific RP-HPLC retention indices for TCDDs are given in Table I and those for HCDDs, H-CDDs, and OCDD are listed in Table II.

As indicated, all 22 TCDD isomers can be fractionated from a sample residue by collecting the column effluent beginning at ~ 11.5 and ending at ~ 17.0 min. The initial stage of TCDD isomer specificity is achieved by collecting the 22 isomers in three separate fractions as shown. TCDD Iso No. 1 (RP-HPLC TCDD isomer fraction no. 1) can contain the following isomers: 1269-, 1469-, 1267-, 1239-, 1268-, 1279-, 1369-, and 1478-TCDD. The TCDD 2378 fraction contains 1246-, 1249-, 2378-, 1236-, 1239-, 1278-, 1237-, 1238-, 1247-, and 1248-TCDD. TCDD Iso No. 2 contains the remaining four isomers: 1378-, 1379-, 1368-, and 1234-TCDD. Preliminary evidence, gained by fortifying samples with roughly equal amounts of all 22 TCDD isomers at approximately the 150 ppb concentration level, has indicated that three of the possible isomers in TCDD Iso No. 1 must be sacrificed in order to ensure quantitative collection of 2378-TCDD in the following fraction. This consequence will be discussed later. Its occurrence is related to the RP-HPLC retention times for the isomers: 1369-TCDD, 1478-TCDD, and one of the pair 1268- or 1279-TCDD having Si rel RT 1.238 (normal-phase silica HPLC retention time

Table II. HCDDs, H-CDDs, and OCDD Retention Indices

CDD isomer	silica- HPLC rel RT ^a	RP- HPLC abs RT ^b	GC-packed column rel RT ^c
HCDDs			
123469-HCDD	1.081	19.23	0.954
123467-HCDD	1.192	19.47	1.077
124679/124689-HCDD	0.958	19.62	0.805
124679/124689-HCDD	0.972	19.70	0.906
123678/123789-HCDD	1.060	20.07	1.103
123679/123689-HCDD	0.970	20.20	0.903
123679/123689-HCDD	1.039	20.23	0.908
123678/123789-HCDD	0.974	20.85	1.016
123478-HCDD	0.941	21.02	1.006 ^d
123468-HCDD	0.890	21.87	0.861
H-CDDs			
1234679-H-CDD		24.00	
1234678-H-CDD		24.65	
OCDD			
		29.40	

^a Silica-HPLC rel RT = retention time relative to 2378-TCDD (± 0.010). ^b RP-HPLC abs RT = absolute retention (± 0.1 min) at peak maximum. ^c GC packed column rel RT = retention time relative to ¹⁴C-123478-HCDD. ^d Native 123478-HCDD elutes slightly later than ¹⁴C-123478-HCDD.

relative to 2378-TCDD). Their retention times are very close to the fraction boundary separating Iso No. 1 and 2378 and are split rather irreproducibly between these fractions. Although these isomers do not necessarily interfere with the quantitation of the isomers expected to the present in the TCDD 2378 fraction, their quantitation essentially becomes impossible. For cases where quantitation of these three TCDDs is required, a second aliquot of sample residue can be fractionated by RP-HPLC in such a manner so as to expand the Iso No. 1 fraction to ensure their collection.

The 10 HCDD isomers are collected in accordance with Figure 3 and Table II. Although isomer-specific HCDD determinations are possible by using essentially the same chromatography procedures described for TCDDs (i.e., RP-HPLC — silica-HPLC — GC), we have not yet applied this system to samples. Similarly, the two H-CDD isomers are collected in a single fraction, as is OCDD.

The RP-HPLC residue fractionation chromatograms in Figure 3 are typical of those associated with particulate samples. The presence of higher chlorinated species, such as H-CDDs and OCDD, can often be observed at this point in the analysis. Although the UV detector has been adjusted for maximum sensitivity for TCDDs, under these conditions a detectable response for HCDDs, H-CDDs, and OCDD is obtained for approximately 5 ng. Similarly, heptachlorodibenzofurans (H-CDFs) and octachlorodibenzofuran (OCDF) may also be observed in the RP-HPLC fractionation. Because of the lack of availability of authenticated chlorinated dibenzofuran (CDFs) standards, we have made no attempt to quantitate these species. Via collection of appropriate RP-HPLC fractions, and capillary GC-EC and GC-LRMS, we have established the possible presence of four H-CDF isomers and OCDF in a variety of particulate samples.

Refractionation of the RP-HPLC TCDD fractions via normal-phase HPLC (silica-HPLC) is the final stage of the sample cleanup prior to GC-LRMS analysis. Normal monitoring of these chromatograms with a UV detector at 0.0 a.u. and 235 nm does not produce observable peaks with the exception of the ¹⁴C-2378-TCDD internal standard. For this reason example chromatograms are omitted. Table I lists the individual TCDD isomers contained in each RP-HPLC TCDD fraction. Included are the RP-HPLC, silica-HPLC, and GC packed column retention indices for each species. By use of

standard containing approximately 10–20 ng each: 2378-TCDD, HCDD(s), H₂CDD(s), and OCDD is no more than 30 μ L of chloroform. In accordance with the chromatogram obtained, appropriate collection zones are established for each of these species (see Discussion section). Following calibration, the injector is rinsed with copious quantities of chloroform, to include multiple consecutive injections of 50 μ L of chloroform into the column to ensure that no residual chlorinated dioxins remain.

The residue is prepared for RP-HPLC fractionation by quantitative transfer to a 0.3-mL Reacti-Vial. Quantitative injection requires complete residue solubility in 30 μ L or less of chloroform. Larger injections of chloroform into this RP-HPLC system severely reduce column efficiency. An aliquot of no more than 30 μ L can be fractionated if the sample residue requires greater amounts of chloroform to be dissolved. Appropriate chlorinated dioxin fractions are collected in 25-mL volumetric flasks, equipped with ground glass stoppers, containing ~1 mL of hexane. The chlorinated dioxins are recovered by addition of 2% (w/v) aqueous sodium bicarbonate. The hexane layer is transferred to a 5-mL glass vial and the aqueous phase is extracted three additional times with ~1 mL of hexane. The combined extracts are then evaporated to dryness under a stream of Pentagas nitrogen. HCDD, H₂CDD, and OCDD fractions are quantitatively transferred to 0.3-mL Reacti-Vials and diluted to appropriate volumes for determination by GC-LRMS.

Regarding the case for an isomer-specific 2378-TCDD determination, additional silica-HPLC fractionation of the RP-HPLC 2378-TCDD fraction is required (see Discussion section). Calibration of the appropriate collection zone is accomplished by injecting approximately 10 ng of 2378-TCDD into the silica-HPLC in 60–80 μ L of hexane and monitoring the chromatogram obtained. Adequate isomer specificity is obtained when the silica-HPLC columns are sufficiently dry so as to provide a 2378-TCDD retention time ranging from a minimum of 12.5 min to maximum of 17 min (24). Following injection of the residue fraction, the chromatogram is monitored and the appropriate 2378-TCDD fraction is collected in a 5-mL glass vial. This fraction is then evaporated to dryness under a stream of Pentagas nitrogen and diluted to appropriate volume for determination by GC-LRMS. This procedure can also be used to collect other TCDD isomers as described in the Discussion section; see Figure 2.

DISCUSSION

The purpose of this paper is to demonstrate the feasibility of using a single multiple-step procedure to accomplish the isomer-specific determination of TCDDs, HCDDs, H₂CDDs, and OCDD at low part per trillion concentrations in a variety of environmental particulate samples. There were two prerequisites for our development of the methodology. First, the sample cleanup must be capable of recovering each of the listed chlorinated dioxin (CDD) groups from a single sample and from a single workup. And second, all procedures must use the least sophisticated and most reliable instrumentation possible so that such analyses could be conducted in the greatest number of analytical facilities. These prerequisites have determined the means by which the described analyses can be accomplished. That is, a neutral or acid extraction procedure must be used. Any treatment of either the sample or its extracts with strong bases is known to cause degradation of the higher chlorinated dioxins (21, 37). In accordance with ease of handling and the general solubility characteristics of higher chlorinated dioxins (least soluble species), continuous benzene extraction was found to be adequate for all particulate samples examined. The selection of packed-column gas chromatography-low-resolution mass spectrometry as opposed to capillary column gas chromatography-high-resolution mass spectrometry represents our attempt to use the least sophisticated instrumentation for CDD determination. Because packed-column GC-LRMS is inherently more subject to possible interference than capillary column GC-HRMS, a more rigorous sample preparation is required. The approach of combining classical extraction and adsorbent clean-up techniques with consecutive RP-HPLC and silica-HPLC residue

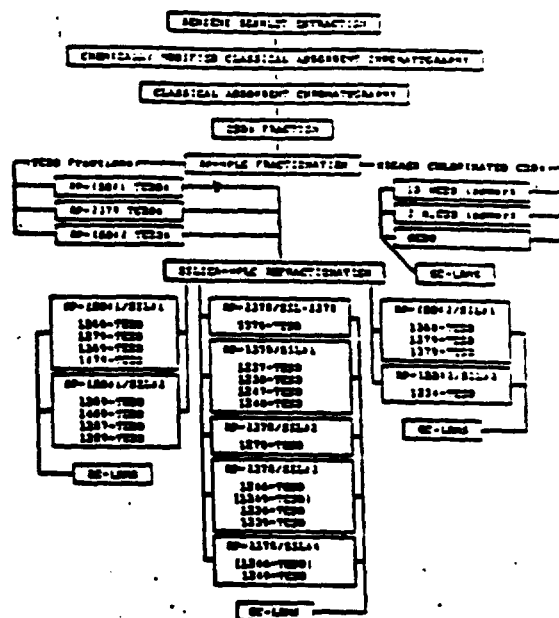


Figure 2. Block diagram for CDD sample preparation.

fractionations can be one solution to this problem. Under these circumstances a significant portion of the method capabilities to prevent MS interferences during the identification and quantification of CDDs is relegated to the cleanup rather than to the final gas chromatographic separation. This can be advantageous when dealing with highly contaminated samples because the chromatographic capacity of the clean-up steps is usually much greater than that of the GC column, especially when capillaries are used. In addition, this approach incorporates the consecutive RP-HPLC and silica-HPLC steps that we have published for the separation and isolation of the 22 TCDD isomers (34). Their described application in this procedure permits the analyst to predetermine which possible TCDD isomers can be present in a given residue fraction. Hence, the necessity of using a capillary GC column to obtain improved TCDD isomer separations is eliminated. This capability may be of utmost importance as the authors are not aware of any published data suggesting that all 22 TCDD isomers can be separated simultaneously using a single capillary GC column. The described methodology will address this problem.

It is to be understood that this procedure has been developed and used for survey purposes on a variety of different environmental particulates. A complete method validation including controls, fortifications, and replicates would be required for each specific matrix before its absolute degree of reliability can be established. The inclusion of isotopically enriched TCDD, HCDD, and OCDD internal standards provide a reasonable degree of reliability under the circumstances of its described uses.

The samples 1.0 g of NBS urban particulate matter, 1.0 g of industrial dust, 1.0 g of electrostatically precipitated fly ash from a municipal burner (fly ash), 18.7 g of Millorganite, and 0.3968 g of European flyash were Soxhlet extracted with benzene for ~16 h and the resulting residues processed through the preliminary liquid chromatographic clean-up steps. Each sample, to include a reagent blank, was fortified with 5–20 ng of isotopically enriched internal standard CDDs (¹⁴C enrichment) prior to analysis. After transfer to a 0.3-mL Reacti-Vial and evaporation of the solvent, all samples yielded

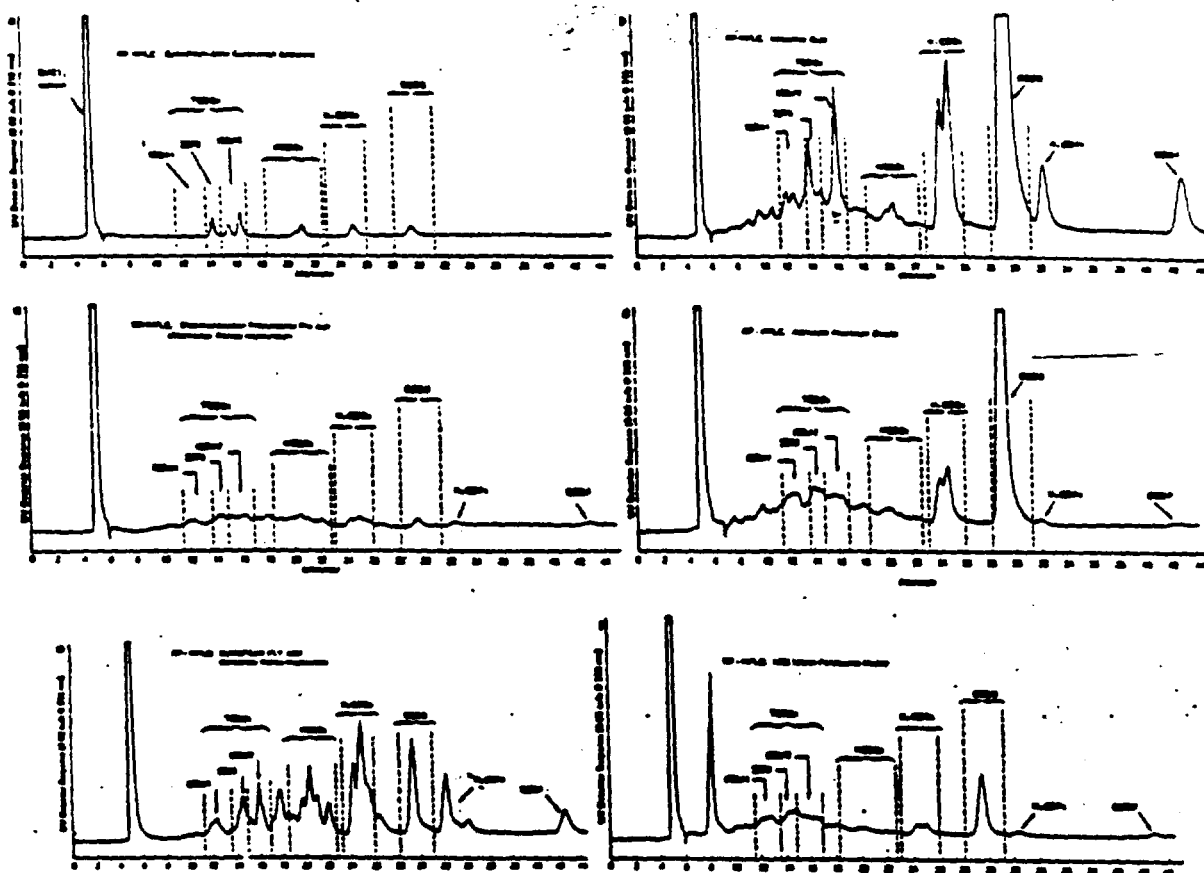


Figure 2. RP-HPLC fractionation chromatograms: (a) calibration standard, (b) industrial dust, (c) electrostatic fly ash, (d) municipal sludge, (e) European fly ash, (f) NBS urban particulates.

this information, appropriate fractions can be collected from the silica-HPLC which permit isomer-specific GC-LRMS identification and quantitation.

The silica-HPLC TCDDs fractionation scheme in Table III is designed to provide maximum isomer-specific information when using our packed-column GC-LRMS analysis, while minimizing the total number of fractions collected. Remembering that the primary goal was to provide the highest quality analytical data for 2378-TCDD, this scheme is adequate. Examination of the GC packed column relative retention times (GC rel RT, TCDD retention time relative to ^{12}C -2378-TCDD) for all TCDDs present in the RP-2378-TCDD fraction indicates that four other TCDDs have GC rel RTs within ± 0.050 (~ 12 s for 4 min absolute retention time for ^{12}C -2378-TCDD) of 2378-TCDD. Arbitrarily defining GC rel RT ± 0.050 as the minimum GC packed column separation for qualitative identification of a TCDD isomer from 2378-TCDD and then direct GC-LRMS analysis of the RP-2378-TCDD fraction would yield a 2378-TCDD value which could include a maximum of four other TCDD isomers (2378-TCDD + 4). However, examination of the silica HPLC relative retention times (SI rel RT, TCDD retention time relative to 2378-TCDD) for these TCDDs indicates that 2378-TCDD is the first isomer to elute. The next isomer to elute is 1237/1238-TCDD (SI rel RT 1.10); however, even at the minimum acceptable silica-HPLC retention time for 2378-TCDD which is ~ 12.5 min, this isomer is separated by ~ 1.75 min. The remaining nine TCDD isomers, other than 2378-TCDD, present in the RP-2378-TCDD fraction can be determined as single isomers with the exception of those in SI Fraction No. 1. Although 1237-,

1238-, 1247-, and 1248-TCDD are essentially baseline separated by silica-HPLC, attempts to collect them in individual fractions under conditions where the species cannot be observed by a UV detector would be difficult. Hence a single fraction is collected for GC-LRMS analysis. As indicated by the respective GC rel RTs, these isomers can be determined as a total for 1237- and 1238-TCDD and a total for 1247- and 1248-TCDD.

Three of the TCDD isomers present in RP-Iso No. 1 are sacrificed in order to ensure maximum recovery of 2378-TCDD in the following RP-HPLC fraction. The consequence of this situation is the possible presence of 1268/1279-TCDD (SI rel RT 1.238), 1369-TCDD, and 1478-TCDD in the RP-2378-TCDD fraction. Regarding their effect upon the isomer-specific determination of 2378-TCDD, it can be observed that no interference occurs by virtue of both their respective silica-HPLC rel RTs and their GC-packed column rel RTs. However, under circumstances where the 1268/1279-TCDD (SI rel RT 1.238) isomer is relatively high in concentration, it could be misidentified as 1237- and 1238-TCDD present in SI Fraction No. 1 of the RP-2378-TCDD fraction. This interference results from similar GC rel RTs for these isomers as indicated in Table III. The 1369/1478-TCDD (SI rel RT 1.220) will not cause any similar interference problems with those TCDDs present in RP-2378-TCDD fraction—SI Fraction No. 1 because of its GC rel RT of 0.802. The remaining isomer, 1369/1478-TCDD (SI rel RT 1.340), if present in high concentration may interfere with 1246/1249-TCDD (SI rel RT 1.411) in RP-2378-TCDD fraction—SI Fraction No. 3.

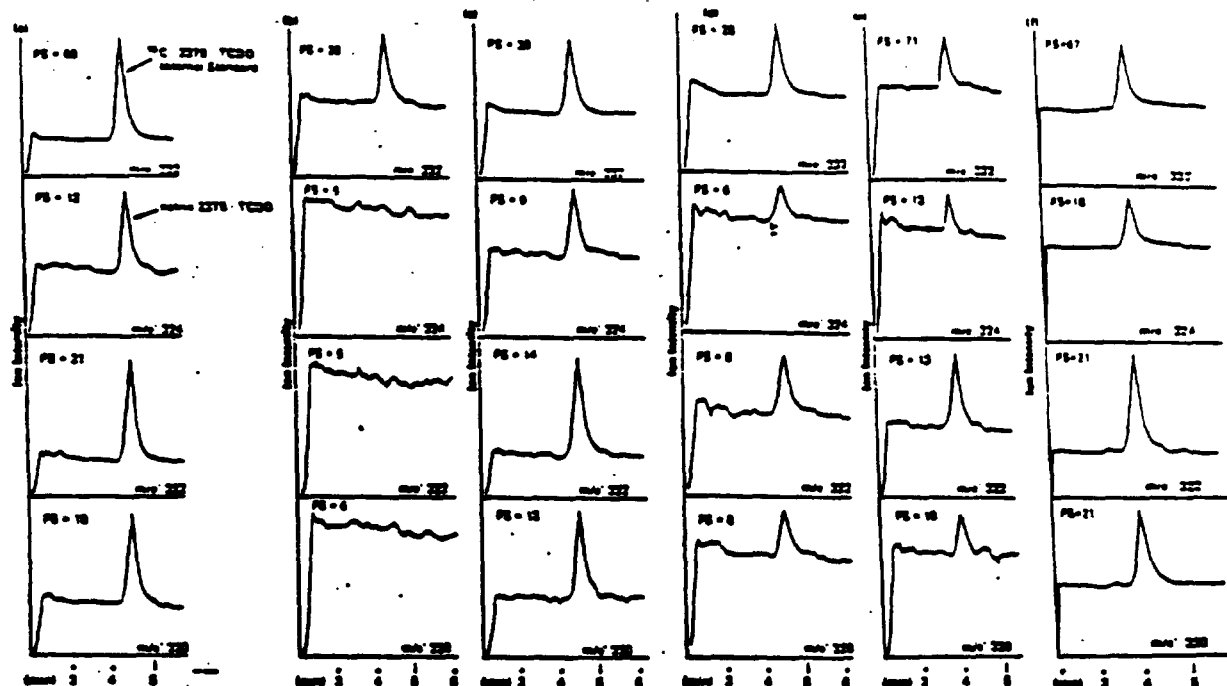


Figure 4. Isomer-specific 2378-TCDD GC-LRMS mass chromatograms: (a) calibration standard, (b) reagent blank, (c) industrial dust, (d) electrostatic fly ash, (e) municipal sludge, (f) European fly ash.

GC-LRMS mass chromatograms for the isomer-specific 2378-TCDD fractions of each particulate sample analyzed are shown in Figure 4. Native 2378-TCDD is monitored at m/e 320, 322, and 324 and ^{13}C -2378-TCDD at 332. The calibration standard (Figure 4a shown) is typical for a 2- μL injection of a reference standard containing 100 pg/ μL of native 2378-TCDD and 500 pg/ μL of ^{13}C -2378-TCDD.

The GC-LRMS mass chromatograms in Figure 5 compare the analysis of the RP-2378-TCDD fraction from electrostatically precipitated fly ash for 2378-TCDD, before and after silica-HPLC refractionation. As a means of ensuring homogeneity, a 2-g portion of sample was processed through the cleanup including RP-HPLC fractionation. At this point the RP-2378-TCDD fraction was divided into two equal portions, each equivalent to 1 g of original sample. One portion was analyzed directly by GC-LRMS as illustrated in Figure 5a. The other portion was further fractionated by silica-HPLC, the S11 Fraction 2378 collected, and this residue analyzed by GC-LRMS (Figure 5b). Comparison of 2378-TCDD quantitation for these residues yields 1500 ppt before silica-HPLC refractionation, and 430 ppt after. The value obtained before silica-HPLC refractionation must be qualified as being the concentration of 2378-HPLC plus four possible unseparated isomers (see Table IV).

Isomer-specific TCDD analysis data for each of the described particulate samples appear in Tables IV and V. Quantitation of TCDDs was accomplished by averaging the observed response at m/e 320, 322, and 324 for all cases except where denoted. Instrumental calibration for all TCDD isomers was based upon the observed responses for a primary standard of 2378-TCDD. The listed concentrations for 2378-TCDD have been corrected for recovery of the ^{13}C -2378-TCDD internal standard as given in Table V. Concentrations given for all other TCDD isomers represent absolute observed values. The limit of detection (LoD) for all species was defined as $2.5 \times$ peak-to-valley noise in a region nearby the expected elution time. Observed concentrations less than the LoD are listed as not detected (ND).

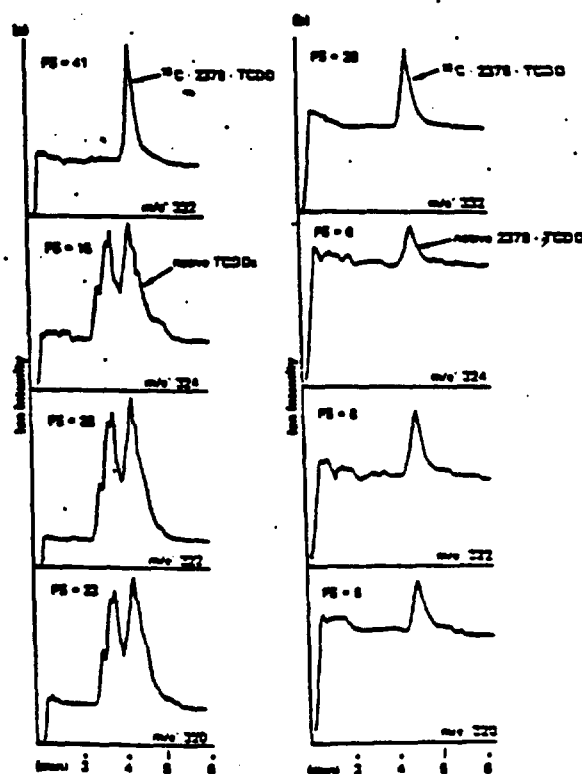


Figure 5. Comparative 2378-TCDD GC-LRMS mass chromatograms for electrostatic fly ash (a) after RP-HPLC (RP-2378 fraction) (b) after silica-HPLC (silica-2378 fraction).

As a means of investigating the degree of reliability associated with the isomer-specific determination of 2378-TCDD in a sample containing equivalent concentrations of all 21 other

Table III. TCDD Isomer Silica-HPLC Fractionation Scheme and Specific Retention Indices

TCDD isomer	silica-HPLC rel RT ^a	Sil collection zone rel RT ^a	GC packed column rel RT ^a
RP-Isol No. 1 Fraction TCDDs			
Sil fraction no. 1		1.180-1.370	
1268/1278-TCDD	1.238 ^c		0.956
	1.291		1.065
1369/1478-TCDD	1.220 ^c		0.802
	1.340 ^c		0.907
Sil fraction no. 2		1.455-1.850	
1269-TCDD	1.702		0.998
1469-TCDD	1.497		0.912
1267/1289-TCDD	1.623		1.081
	1.795		1.200
RP-2378 Fraction TCDDs			
Sil fraction 2378		0.950-1.050	
2378-TCDD	1.000		1.006 ^d
Sil fraction no. 1		1.050-1.244	
1237/1238-TCDD ^e	1.100		0.979
	1.128		0.990
1247/1248-TCDD ^e	1.154		0.854
	1.199		0.857
Sil fraction no. 2		1.244-1.300	
1278-TCDD	1.288		0.893
Sil fraction no. 3		1.300-1.385	
1246/1249-TCDD	1.328		0.896
1236/1239-TCDD	1.356		1.037
	1.350		0.969
Sil fraction no. 4		1.385-1.450	
1246/1249-TCDD	1.411		0.898
RP-Isol No. 2 Fraction TCDDs			
Sil fraction no. 1 ^f		0.900-1.050	
1368-TCDD	0.940		0.729
1379-TCDD	0.977		0.771
1378-TCDD	1.000		0.858
Sil fraction no. 2 ^f		1.210-1.288	
1234-TCDD	1.248		0.960

^a Silica-HPLC rel RT = retention time relative to 2378-TCDD (± 0.010). ^b GC packed column rel RT = retention time relative to ¹⁴C-2378-TCDD (± 0.005). ^c See text for recovery information. ^d Native 2378-TCDD elutes slightly later than ¹⁴C-2378-TCDD. ^e Related isomers typically reported as a total. ^f Fractions typically combined prior to GC-LRMS analysis.

TCDD isomers, we intentionally fortified a second portion of municipal sludge with each TCDD isomer at the levels shown in Table VI. Neither 1237- or 1238-TCDD was added due to their natural presence at 230 ppb (see Table V). Analysis of the fortified sample yielded the recovery data shown in Table VI. Regarding the 2378-TCDD data, the amount found was corrected for the recovery of the ¹⁴C-2378-TCDD and also for the 20 ppb natural 2378-TCDD previously observed in

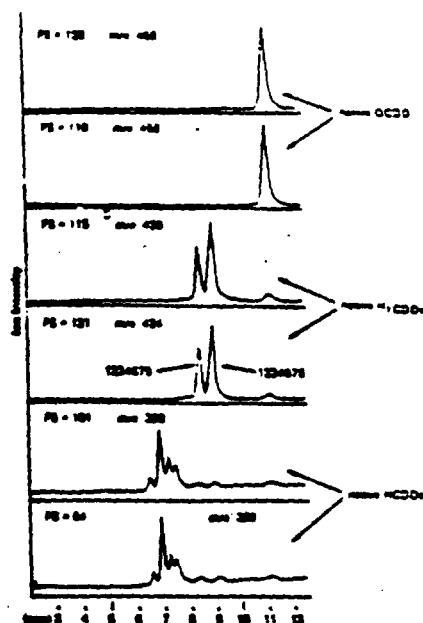


Figure 6. Higher chlorinated dioxin GC-LRMS mass chromatograms for electrostatic fly ash.

the sample. These data indicate that no other TCDD isomer interferes with the determination of 2378-TCDD when this analytical procedure is used. Recovery values given for all other TCDD isomers represent absolute observed values and were corrected for natural levels when necessary as listed in Table VI.

Typical temperature programmed GC-LRMS mass chromatograms for the determination of higher chlorinated dioxins appear in Figure 6. For the analysis of electrostatically precipitated fly ash the RP-HPLC HCDDs, H₂CDDs, and OCDD fractions were combined prior to GC-LRMS examination (see Figure 3c). As a means of overcoming problems associated with samples having relatively large amounts of native chlorinated dioxins compared to the 1-20 ng of fortified internal standards, a complete method validation study was conducted for HCDDs, H₂CDDs, and OCDD ranging from 50 ppb to 10 ppm ($\mu\text{g/g}$) and from 10 ppb to 5 ppb for 2378-TCDD. The control particulate sample used was a sandy loam soil, to which was added ~150 μL of Mobile 1 synthetic engine lubricant per 20 g, as a means of increasing the total organics content to better simulate typical particulates. The following native CDD standards were used for sample fortification: 2378-TCDD, 123678-HCDD, 123679/123689-HCDD (Sil rel RT 1.039), 1234678-H₂CDD, and OCDD. The results of this

Table IV. Chlorinated Dioxins Observed in Environmental Particulate Samples

CDDs	reagent blank, ng	parts per billion				
		industrial dust	electrostatic flyash	municipal sludge	European flyash	NBS urban particulates
2378-TCDD + 4 isomers ^a	ND (0.06)	...	1.5 ^b	0.12 (0.12) ^c
other TCDDs (17 isomers)	ND (0.04)	0.16 (0.08)
HCDDs ^d (10 isomers)	ND (0.18)	ND (14)	14	2.1	550 ^d	2 (2)
1234679-H ₂ CDD ^e	ND (0.14)	200	11	14	470	16
1234678-H ₂ CDD ^e	ND (0.14)	220	17	15	870	18
OCDD ^e	ND (0.29)	4000	30	180	850	210

^a RP-HPLC RP-2378 fraction analyzed directly by GC-LRMS and not isomer specific as described in text. ^b Sample fully fractionated for isomer-specific results given in Table V. ^c Observed values without correction run as part of validation work reported in Table VII. ^d For "semi" isomer specific see Table VIII. ^e ¹⁴C-2378-TCDD recovery 78% and value listed has been corrected, see Table V for others, and ND = compound not detected at limit of detection in parentheses and no parentheses indicates detected signal > 10x limit of detection.

Table V. Isomer-Specific TCDD Analysis of Environmental Particulate Samples

TCDD isomer	reagent blank, pg	parts per trillion			
		industrial dust	electrostatic flyash	municipal sludge	European flyash
2378-TCDD ^a	ND (40)	1100	430 (110)	20 (2)	2300
1269-TCDD	ND (20)	ND (40)	190 (60)	ND (2)	1000 (140)
1469-TCDD	ND (20)	ND (50)	ND (50)	ND (2)	250 (140)
1267/1269-TCDD SU rel RT 1.623	ND (20)	ND (50)	100 (60)	ND (2)	300 (140)
1267/1269-TCDD SU rel RT 1.795	ND (20)	ND (50)	120 (60)	ND (2)	500 (140)
1268/1279-TCDD SU rel RT 1.233	ND (30) ^b	190 (90) ^c	1000 ^c
1268/1279-TCDD SU rel RT 1.291	ND (30)	ND (50)	310 (90)	3 (3) ^d	1500
1369/1478-TCDD SU rel RT 1.220
1369/1478-TCDD SU rel RT 1.340
1278-TCDD	ND (60)	ND (40)	ND (80)	ND (3)	3100
1236/1239-TCDD SU rel RT 1.356	ND (60)	ND (60)	250 (110)	ND (3)	1500
1236/1239-TCDD SU rel RT 1.350	ND (60)	ND (60)	150 (110)	ND (3)	800 (400)
1227/1235-TCDD SU rel RT 1.100	ND (60)	240 (50) ^e	720 ^e	230 ^e	8500 ^e
1227/1235-TCDD SU rel RT 1.123					
1246/1249-TCDD SU rel RT 1.323	ND (60)	ND (60) ^e	730 (110) ^e	ND (3) ^e	2000 ^e
1246/1249-TCDD SU rel RT 1.411					
1247/1248-TCDD SU rel RT 1.154	ND (60)	140 (50)	310 (70)	8 (2)	6900
1247/1248-TCDD SU rel RT 1.199					
1378-TCDD	ND (20)	560 (110)	1370 (150)	23 (5)	13200
1379-TCDD	ND (20)	1340	1160 (150)	13 (5)	7000
1368-TCDD	ND (20)	2780	1320 (150)	13 (5)	16200
1234-TCDD	ND (20)	180	870 (150)	ND (30)	2100
total TCDDs	ND	6340	7750	310	69800
¹⁴ C-2378-TCDD % recovery	63%	59%	54%	61%	56%

^a Corrected for ¹⁴C-2378-TCDD recovery and all other isomers are absolute observed. ^b = not recovered as described in text. ^c Observed but recovery questionable. ^d Detected on m/e 322 only. ^e Possible isomer interference as described in text.

Table VI. Isomer-Specific TCDD Analysis of Municipal Sludge after Fortification

TCDD isomer	concn in ppt		% recovery
	added	found	
2378-TCDD	143	140	98 ^a
1269-TCDD	150	108	72
1469-TCDD	186	122	73
1267/1269-TCDD SU rel RT 1.623	150	126	84
1267/1269-TCDD SU rel RT 1.795	171	145	85
1268/1279-TCDD SU rel RT 1.233	137 ^b	...
1268/1279-TCDD SU rel RT 1.291	140	69	49
1369/1478-TCDD SU rel RT 1.220	143
1369/1478-TCDD SU rel RT 1.340	151
1278-TCDD	160	104	65
1236/1239-TCDD SU rel RT 1.356	147	103	70
1236/1239-TCDD SU rel RT 1.350	148	80	55
1227/1235-TCDD SU rel RT 1.100	} c	(180) ^d	
1227/1235-TCDD SU rel RT 1.123			
1246/1249-TCDD SU rel RT 1.323	141	} 220 ^e	75
1246/1249-TCDD SU rel RT 1.411	151		
1247/1248-TCDD SU rel RT 1.154	131	} 203 ^e	69
1247/1248-TCDD SU rel RT 1.199	163		
1378-TCDD	171	151	88
1379-TCDD	171	138	81
1368-TCDD	101	45	45
1234-TCDD	143	122	85

^a Corrected for recovery of ¹⁴C-2378-TCDD (72%) and native 2378-TCDD present given in Table V, all other isomers are absolute observed. ^b = not recovered as described in text. ^c Total not added. High native concentration given in Table V. ^d Absolute amount observed in this sample. ^e Total.

study appear in Table VII. These data indicate that the average recoveries of HCDDs, H₂CDDs, and OCDD over the described concentrations range are reasonably constant and are between 70 and 80%. Because typical particulate samples contain higher chlorinated CDDs within this range, recovery factors derived from the validation can be used. Since ¹⁴C-

labeled internal standards are added to all samples, whenever very low native concentrations are observed appropriate correction factors can be applied. Note that recovery values reported for TCDD have been corrected for the observed ¹⁴C-2378-TCDD internal standard recoveries after RP-HPLC fractionation.

Table VII. Chlorinated Dioxin Recovery and Precision Data for Fortified Sandy Loam Soil^a

sample no.	2378-TCDD ^b			HCDD			H.CDD			OCDD		
	added, ppur	found, ppur	%	added, ppur	found, ppur	%	added, ppur	found, ppur	%	added, ppur	found, ppur	%
1	10	13	130	50	30	60	50	46	92	200	160	80
2	20	25	140	100	72	72	100	73	73	400	320	80
3	20	21	105	100	87	87	100	65	65	400	260	65
4	50	49	98	250	160	64	250	170	68	1000	730	73
5	50	45	90	250	180	72	250	200	80	1000	820	82
6	50	51	102	250	170	68	250	200	80	1000	780	78
7	50	53	106	250	170	68	250	170	68	1000	720	72
8	50	50	100	250	190	76	250	210	84	1000	850	85
9	50	50	100	250	180	72	250	160	64	1000	700	70
10	50	47	94	250	180	72	250	180	72	1000	890	89
11	50	52	104	250	170	68	250	160	64	1000	890	89
12	100	97	97	500	410	82	500	430	86	2000	1900	95
13	100	109	109	500	440	88	500	460	92	2000	2060	103
14	5000	5350	107	1 x 10 ⁴	8.1 x 10 ³	81	5 x 10 ³	4.5 x 10 ³	90	10 x 10 ³	8.4 x 10 ³	84
15	5000	5400	108	1 x 10 ⁴	9.1 x 10 ³	91	5 x 10 ³	4.7 x 10 ³	94	10 x 10 ³	9.0 x 10 ³	90
\bar{x} all ^c			106			73			78			80
σ all ^c			13			10			11			11
\bar{x} prec ^d	50	49.6	99.2	250	173	69	250	181	72	1000	751	75
σ prec ^d		2.6	5.2		10.4	6.0		19.6	10.8		69.4	9.2

^a Data for all species obtained by GC-LRMS analysis of appropriate RP-HPLC fractions. 2378-TCDD values corrected for ¹⁴C-2378-TCDD internal standard recovery, other CDDs are absolute observed. ^b Corrected for ¹⁴C-2378-TCDD where average recovery was 59.8% for all samples. ^c \bar{x} all and σ all represent the mean and standard deviation of all samples. ^d \bar{x} prec and σ prec represent the mean and standard deviation of samples 4-11 to determine precision of the analysis.

Table VIII. "Semi" Isomer-Specific HCDD Analysis Data for European Flyash, Absolute Values Reported

HCDD isomer ^a	parts per billion	
	reagent blank	European Flyash
124679/124689-HCDD SU rel RT 0.958	ND (0.13) ^{b,c}	82 ^c
124679/124689-HCDD SU rel RT 0.972		
123488-HCDD	ND (0.13)	9 (9)
123679/123689-HCDD SU rel RT 0.970	ND (0.13) ^c	260 ^c
123679/123689-HCDD SU rel RT 1.039		
123469-HCDD		
123478-HCDD	ND (0.13) ^c	110 ^c
123678/123789-HCDD SU rel RT 0.974		
123678/123789-HCDD SU rel RT 1.060	ND (0.13) ^c	85 (9) ^c
123467-HCDD		

^a HCDD SU rel RT = retention time relative to 2378-TCDD by silica-HPLC (Table II). ^b ND (0.13) is not detected with limit of detection in ppb based on flyash sample size. ^c Total.

GC-LRMS analysis data for higher chlorinated CDDs appear in Tables IV and VIII. Table VIII illustrates a format for HCDD determination that is "semi"-isomer specific. In this case, the total RP-HCDDs fraction was analyzed directly by packed-column GC-LRMS. However, because GC rel RTs have been experimentally determined (see Table II) for all 10 individual HCDD isomers, we can separate the HCDDs observed into five distinct groups. Within each group only a limited number of isomers are possible. These analyses are accomplished by using isothermal column condition (~270 °C) so as to maximize the separation power of the column and to improve relative retention time measurements.

CONCLUSIONS

Although this paper demonstrates the applicability of a multiple-step procedure to isomer-specifically determine a variety of CDDs in environmental particulate samples, we have also applied the technique to many other matrices successfully. Simple modification of the preliminary matrix extraction has permitted the analysis of tissues, human milk, vegetable matter, chemical products, and wastes without sacrificing high sensitivity or isomer specificity. This procedure, utilizing packed-column GC-LRMS, has provided reliable results for several heavily contaminated matrices where the combination

of a less sophisticated cleanup followed by both packed and capillary column GC-HR MS has failed. Interested individuals may request a more thorough discussion of the method development experiments from the authors.

ACKNOWLEDGMENT

The authors express their gratitude to O. Hutmeger for graciously supplying the European fly ash sample and to R. Bumb, W. Crummett, and V. Stenger for their help in preparing this manuscript.

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RECEIVED for review January 28, 1980. Resubmitted May 14, 1980. Accepted July 31, 1980.

Secondary Ion Mass Spectra of Diquaternary Ammonium Salts

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Molecular dications emitted by momentum transfer processes are observed in secondary ion mass spectra (SIMS) of diquaternary ammonium salts. The relationship between molecular structure and the observation of dications is explored. Large interchange separations, corresponding to lessened intramolecular coulombic repulsions, are observed to correlate with dication detection. Fragmentation with charge separation is facilitated by small interchange distances and can preclude observation of the dication. Electron attachment to yield the monocation is an alternative to dication emission when the structure of the dication facilitates reduction. This occurs, for example, for the herbicide diquat (*N,N'*-ethylene-2,2'-bipyridyl dibromide) which is detected as its monocation. Complete spectra of diquaternaries can be taken with nanogram size samples.

Secondary ion mass spectrometry (SIMS) has recently been shown to be a sensitive method for the characterization of organic salts (1-6). Reported here is the observation of intact organic dications emitted from diquaternary ammonium salts upon sputtering. This constitutes the first observation of multiply charged organic molecular ions in SIMS. The result is of interest with regard to both analytical applications of SIMS and the fundamentals of ionization during sputtering. Specifically, some biologically important compounds, such as the herbicides paraquat and diquat and the curare alkaloids, have the diquaternary structure, so that SIMS may facilitate their characterization. In addition, studies on organic dications reflect the degree to which electron attachment occurs during sputtering. This process yields observable charged products for dications, but neutrals are sputtered when monocations are reduced during ion bombardment.

EXPERIMENTAL SECTION

All compounds were synthesized by using standard methods for the preparation of quaternary ammonium salts. The organic salts were burnished onto a 1 cm² roughened foil of either silver

or platinum prior to SIMS analysis using argon primary ions at 8 keV and 0.3-0.5 nA primary ion current. Beam diameter was approximately 1 mm and pressures in the ultra-high-vacuum chamber remained below 1×10^{-8} torr during the course of the experiments.

All spectra were taken with Riber SIMS system using a quadrupole mass analyzer, Channeltron electron multiplier, and pulse-counting electronics.

Intercharge distances were measured by using Dreiding models; charge localization on nitrogen was assumed and the maximum distance in the unstrained molecule is reported. Intercharge distances (*r*) were used to calculate coulombic repulsive energies (*T*) from T (eV) = $14.6/r$ (Å).

RESULTS AND DISCUSSION

The SIMS spectrum of *N,N'*-bis(dimethyl)-4,4'-trimethylenedipiperidine diiodide (1) is shown in Figure 1. This spectrum provides both the molecular weight (inferred from the highest mass doubly charged ion, 268²⁺) and structural information on the compound. Emission of the doubly charged species is confirmed by the observation of the ¹³C isotope peak one-half mass unit above the dication peak (*m/z* 134.5 in Figure 2). Changing the counterion does not affect the SIMS spectrum; for example, the dibromide and diiodide of compound 1 gave identical SIMS spectra.

Analogous results were obtained for *N,N'*-bis(ethyl-methyl)-4,4'-trimethylenedipiperidine diiodide (2) and for the aromatic compounds *N,N'*-bis(trimethyl)-4,4'-methylenedianiline diiodide (3) and *N,N'*-bis(dimethylethyl)-4,4'-methylenedianiline diiodide (4). The spectrum of compound 3 is shown in Figure 3; the dication, 234²⁺ at *m/z* 142 is of relatively low abundance, but its ¹³C isotope is well resolved in high-resolution scans.

A considerable number of diquaternary salts (5-19, Table I) did not exhibit observable dications. Compounds 18 and 19, while they did not yield molecular dications, did show the corresponding singly charged ions in their SIMS spectra. Compounds 5-17 may fail to exhibit dications because they fragment by a favorable charge separation route, $M^{2+} \rightarrow M_1^{+} + M_2^{+}$. This is indicated by the absence of both singly and doubly charged molecular ions for these samples.

APPENDIX II

temperature of the water bath to 85 to 90°C. Concentrate the extract as in section 11.2.6 except use hexane to prewet the column. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of hexane.

11.2.8 Add a clean boiling chip to the concentrator tube and attach a two-ball micro-Snyder column. Premix the column by adding about 1 mL of hexane to the top. Place the micro-K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5 to 10 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of the liquid reaches about 0.5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes. Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with 0.2 mL hexane. Proceed to section 11.3.2. If further processing is to be delayed, the extract should be quantitatively transferred to a Teflon sealed screw-cap vial and store refrigerated and protected from light.

11.2.9 Fill the sample bottle with water to the mark and measure the volume to the nearest 10 mL in a 1 L graduated cylinder.

11.3 Column Chromatograph

11.3.1 Column Preparation

11.3.1.1 Column 1: Place 1.0 g of silica gel into a 1 cm x 20 cm column and tap the column gently to settle the silica gel. Add 2 g sodium hydroxide-impregnated silica gel, 1 g silica gel, 4.0 g of sulfuric acid-impregnated silica gel, and 2 g silica gel. Tap column gently after each addition.

11.3.1.2 Column 2: Place 6.0 g of alumina into a 1 cm x 30 cm column and tap the column gently to settle the alumina. Add a 1-cm layer of purified sodium sulfate to the top of the alumina.

11.3.1.3 Add hexane to each column until the packing is free of channels and air bubbles. A small positive pressure (5 psi) of clean nitrogen can be used if needed.

11.3.2 Quantitatively transfer the hexane sample extract from the concentrator tube to the top of the silica gel in Column 1. Rinse the concentrator tube with two 0.5 mL portions of hexane; transfer rinses to Column 1.

- 11.3.3 With 90 mL of hexane, elute the extract from Column 1 directly into Column 2 containing alumina and sodium sulfate.
- 11.3.4 Add 20 mL of hexane to Column 2 and elute until the hexane level is just below the top of the sodium sulfate; discard the eluted hexane.
- 11.3.5 Add 20 mL of 20% methylene chloride/80% hexane (volume/volume) to Column 2 and collect the eluate.
- 11.3.6 Reduce the volume of the eluate with a gentle stream of filtered dry nitrogen. When the volume of the eluate is about 1 to 2 mL, transfer the eluate to the Carbowack column (Section 11.4.4). Rinse the eluate container with two 0.5 mL portions of hexane; transfer the rinses to the Carbowack column. CAUTION: Do not evaporate the sample extract to dryness. NOTE: The carbowack cleanup is not required for water samples unless needed to meet detection sensitivity criteria.

11.4 Carbowack Column Chromatography Procedure

- 11.4.1 Thoroughly mix 3.6 g of Carbowack C (or equivalent) with 16.4 g of Celite 545 (or equivalent) in a 40 mL vial and activate by heating in an oven at 130°C for 6 hours. Store in a desiccator. CAUTION: Check each new batch of mixed Carbowack/Celite to ensure TCDD recovery of >50%. Subject the low level concentration calibration solution to this procedure and measure the quantity of labeled and unlabeled 2,3,7,8-TCDD.
- 11.4.2 Insert a small plug of glass wool into a disposable pipet approximately 15 cm long by 7 mm O.D. Apply suction with a vacuum aspirator attached to the pointed end of the pipet, and add the Carbowack/Celite mixture until a 2 cm packing is obtained.
- 11.4.3 Pre-elute the column with:
- 11.4.3.1 2 mL toluene
 - 11.4.3.2 1 mL of mixture of 75% (by volume) methylene chloride, 20% methanol and 5% benzene
 - 11.4.3.3 1 mL of 50% (by volume) cyclohexane and 50% methylene chloride
 - 11.4.3.4 2 mL of hexane
- 11.4.4 While the column is still wet with hexane add the sample extract from section 11.2.6. Elute the column with the following sequence of solvents and discard the eluates.

11.4.4.1 2 mL hexane

11.4.4.2 1 mL of 50% (by volume) cyclohexane and 50% methylene chloride

11.4.4.3 1 mL of 75% (by volume) methylene chloride, 20% methanol and 5% benzene

11.4.5 Elute with 2 mL of toluene and collect the eluate, which contains the TCDD. Transfer the rinses to a 1-mL amber mini-vial with conical reservoir with further concentration as necessary. CAUTION: Do not evaporate the sample extract to dryness.

11.3.6 Store the sample extract in the dark at 4°C until just before GC/MS analysis.

11.5 GC/MS Analysis

11.5.1 Remove the sample extract or blank from storage and allow it to warm to ambient laboratory temperature. With a stream of dry, filtered nitrogen, reduce the extract/blank volume to near dryness. Immediately before GC/MS analysis, add 5 µL of the 10 ng/µL recovery standard solution and adjust the extract or blank volume to 50 µL with isooctane.

11.5.2 Inject a 2-µL aliquot of the extract into the GC, operated under conditions previously used (Section 9) to produce acceptable results with the performance check solution.

11.5.3 Acquire mass spectral data for the following selected characteristic ions: m/z 259, 320, and 322 for unlabeled 2,3,7,8-TCDD; m/z 328 for ³⁷Cl₄-2,3,7,8-TCDD; and m/z 332 and 334 for ¹³C₁₂-2,3,7,8-TCDD and ¹³C₁₂-1,2,3,4-TCDD. Use the same data acquisition time and MS operating conditions previously used (Section 9.2.6) to determine response factors.

11.6 Identification Criteria. NOTE: Refer to Exhibit E, Section 7, for application of identification criteria.

11.6.1 Retention time (at maximum peak height) of the sample component must be within 3 seconds of the retention time of the ¹³C₁₂-2,3,7,8-TCDD. Retention times are required for all chromatograms, but scan numbers are optional. These parameters should be printed next to the appropriate peak.

11.6.2 The integrated ion currents detected for m/z 259, 320, and 322 must maximize simultaneously. If there are peaks that will affect the maximization or quantitation of peaks of interest, attempts should be made to narrow the scan window to eliminate the interfering peaks. This should be reported on a separate chromatogram.

- 11.6.3 The integrated ion current for each analyte and surrogate compound ion (m/z 259, 320, 322 and 328) must be at least 2.5 times background noise and must not have saturated the detector; internal standard ions (m/z 332 and 334) must be at least 10 times background noise and must not have saturated the detector.
- 11.6.4 Abundance of integrated ion counts detected for m/z 320 must be $\geq 67\%$ and $\leq 90\%$ of integrated ion counts detected for m/z 322.
- 11.6.5 Abundance of integrated ion counts detected for m/z 332 must be $\geq 67\%$ and $\leq 90\%$ of integrated ion counts detected for m/z 334.
- 11.6.6 The recovery of the internal standard $^{13}\text{C}_{12}$ -2,3,7,8-TCDD should be within a 40 percent to 120 percent recovery window. This is an advisory limit only, an action window may be set when sufficient data is available.

12. CALCULATIONS

12.1 Concentration

- 12.1.1 Calculate the concentration of 2,3,7,8-TCDD using the formula:

$$C_x = \frac{A_x \cdot Q_{is}}{A_{is} \cdot RPF_n \cdot W}$$

- where C_x = 2,3,7,8-TCDD concentration in ug/kg or ug/L
- A_x = the sum of integrated ion abundance detected for m/z 320 and 322
- A_{is} = the sum of integrated ion abundances detected for m/z 332 and 334 (characteristic ions of $^{13}\text{C}_{12}$ -2,3,7,8-TCDD, the internal standard)
- Q_{is} = quantity (in ug) of $^{13}\text{C}_{12}$ -2,3,7,8-TCDD added to the sample before extraction
- RPF_n = calculated mean response factor for unlabeled 2,3,7,8-TCDD relative to $^{13}\text{C}_{12}$ -2,3,7,8-TCDD
- W = weight (in g) of wet soil or sediment sample or volume of water extracted (in mL).

12.1.2 If the calculated concentration of unlabeled 2,3,7,8-TCDD exceeds 100 ug/kg for soil/sediment or 1 ug/L for water, which is the maximum concentration of the concentration calibration solutions, the linear range may have been exceeded, and a smaller aliquot of that sample must be analyzed. Accurately weigh to three significant figures a 1-g aliquot of the wet soil/sediment or measure a 100 mL aliquot of water. Add the 1.5 mL acetone dilution of 100 uL of the sample fortification solution (Section 7.8), just as for the larger sample aliquot. Extract and analyze.

12.1.3 Calculate the concentration of the internal standard $^{13}\text{C}_{12}$ -2,3,7,8-TCDD using the formula:

$$C_{is} = \frac{A_{is} \cdot Q_{rs}}{A_{rs} \cdot RF_i \cdot W}$$

where

C_{is} = concentration of $^{13}\text{C}_{12}$ -2,3,7,8-TCDD in ug/kg or ug/L

A_{is} = sum of integrated ion abundances for m/z 332 and 334 for $^{13}\text{C}_{12}$ -2,3,7,8-TCDD

A_{rs} = sum of integrated ion abundances for m/z 332 and 334 for $^{13}\text{C}_{12}$ -1,2,3,4-TCDD

Q_{rs} = quantity (in ng) of $^{13}\text{C}_{12}$ -1,2,3,4-TCDD added to the sample before injection

RF_i = calculated mean response factor for $^{13}\text{C}_{12}$ -1,2,3,4-TCDD

W = weight (in g) of wet soil or sediment sample or volume of water extracted (in mL).

12.2 Estimated Maximum Possible Concentration — For samples in which no unlabeled 2,3,7,8-TCDD was detected, calculate the estimated maximum possible concentration, which is the concentration required to produce a signal with peak height of 2.5 times the background signal level. The background level is determined by measuring the range of the noise (minimum to maximum) for either m/z 320 or 322 in the appropriate region of the SICP (as defined in section 1.3.11), multiplying that noise height by 2.5, and relating the product height to an estimated concentration that would produce that product height.

Use the formula:

$$MPC = \frac{2.5 \cdot A_x \cdot Q_{is}}{A_{is} \cdot RF_n \cdot W}$$

where MPC = estimated maximum possible concentration of unlabeled 2,3,7,8-TCDD required to produce A_x in ug/kg or ug/L

A_x = peak height for either m/z 320 or 322 within + 5 scans of the internal standard peak used to measure A_{is}

A_{is} = peak height of the appropriate ion characteristic of the internal standard, m/z 332 when m/z 320 is used to determine A_x , and m/z 334 when m/z 322 is used to determine A_x

Q_{is} , RF and W retain the definitions previously stated in Section 12.1.1

12.4 The relative percent difference (RPD) is calculated as follows: (See Section 5.1.1, Exhibit E.)

$$RPD = \frac{S_1 - S_2}{\text{Mean Concentration}} \times 100 = \frac{|S_1 - S_2|}{\frac{S_1 + S_2}{2}} \times 100$$

S_1 and S_2 represent sample and duplicate sample results.

12.6 Percent Recovery of 2,3,7,8-TCDD in spiked field blanks =

$$\frac{\text{concentration found}}{\text{concentration added}} \times 100$$

12.7 Percent Recovery of internal standard, $^{13}\text{C}_{12}$ -2,3,7,8-TCDD =

$$\frac{\text{concentration found}}{\text{concentration added}} \times 100$$

$$12.8 \text{ Standard deviation} = S = \sqrt{\frac{\sum_{i=1}^N (X_i - \bar{X})^2}{N - 1}}$$

12.9 Percent relative standard deviation =

$$\frac{\text{Standard Deviation}}{\text{Mean}} \times 100 = \frac{S}{\bar{X}} \times 100$$

APPENDIX III

- 1.7.1.2 Immediately after weighing the sample for extraction, weigh 5-10 g of the sediment into a tared crucible. Determine the percent moisture by drying overnight at 105°C. Allow to cool in a desiccator before weighing. Concentrations of individual analytes will be reported relative to the dry weight of sediment.

$$\frac{\text{gm of sample} - \text{gm of dry sample}}{\text{gm of sample}} \times 100 = \% \text{ moisture}$$

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APPENDIX IV

Tetra-Octa CDD/CDF Scan Quantitation Protocol and Analytical Standards

- Minimal Requirements for Bidders

Analytical Standards

- 2378 TCDD, $^{13}\text{C}_{12}$, $^{37}\text{Cl}_4$
- 2378 TCDF
- Mixture of TCDD isomers to verify column resolution *
- OCDD, $^{13}\text{C}_{12}$ -OCDD
- Mix of Penta CDD/CDF, Hexa CDD/CDF, Hepta CDD/CDF to establish RT windows for spiking. *Continuing calibrations must be within RT windows established.*

Quantitation

Quantitate TCDD, TCDF, Penta CDD, Penta CDF, Hexa CDD, Hexa CDF
against $^{13}\text{C}_{12}$ -2378-TCDD

(Quantitate TCDF, Penta CDF, and Hexa CDF against $^{13}\text{C}_{12}$ -TCDF, ~~if available~~)

Quantitate Hepta CDD, Hepta CDF, OCDD, OCDF against $^{13}\text{C}_{12}$ -OCDD

Qualify data as "estimated" concentrations with tentative identifications unless you have access to pure isomer standards (i.e., all 38 TCDF isomers, etc.)

WA-56K357
* Column resolution should meet Dioxin IFB ~~WA84-A002~~ criteria i.e. 25% valley or lower between 2,3,7,8-TCDD and it's nearest neighbor in SIC display (Appendix VII).

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APPENDIX V

DELIVERABLES REQUIRED FOR GC/MS DIOXIN/FURAN ANALYSIS

A. SAMPLE PREPARATION AND METHOD DOCUMENTATION

- (1) "Cookbook" style step-by-step method including instrument/conditions, type and source of reagents.
- (2) Analyst bench records describing dilutions, weighings and any unusual occurrences during prep, extraction or clean up.
- (3) Calculations and method used in determination of percent lipids and percent solids (where applicable).

B. DIOXIN/FURAN QUANTITATION AND IDENTIFICATION DOCUMENTATION

- (1) Detailed explanation of the quantitation and identification procedure used for all isomer classes and specific isomers.
- (2) List of criteria for positive identification of 2,3,7,8-TCDD and 2,3,7,8-TCDF.
- (3) Example calculations of response ratios, sample results and detection limits.
- (4) Simultaneous display/offset SICs and peak areas of native, $^{13}\text{C}_{12}$ - and $^{37}\text{Cl}_4$ -2,3,7,8-TCDD in all samples and QC, including blanks.
- (5) Simultaneous display/offset SICs and peak areas of ions monitored for each PCDD/PCDF class.
- (7) List of exact ion masses for each isomer/class, current and historical response factors and retention times for positive ID.
- (8) Simultaneous display/offset SICs to check for polychlorinated diphenylethers which may co-elute with the furans.
- (9) Simultaneous display/offset SICs of M/Z 257, 259 in samples with positive 2, 3, 7, 8-TCDD content.
- (10) Simultaneous display/offset SICs and peak areas of ions monitored, for all standards used, for each PCDD/PCDF class. Include a listing of response ratios, ion ratios and amount of each standard used.

(11) Chronological List (date/time) of all standards, native spikes, method blanks, duplicates, samples, reanalyses etc.

(12) Completed copy (including sample condition) of SAS packing List.

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APPENDIX VI

CASE 1

PCDD/PCDF Concentration (PPT) as Dry Weight

ISOMER OR HOMOLOG	DATE:	ALIQOT WT. (g)	DATE:	ALIQOT WT. (g)	PRECISION AS RPD	PRECISION LIMITS	COMMENTS
	Samp. #		Samp. #				
2,3,7,8-TCDF							
3/CI-2,3,7,8-TCDF							
% Recovery							
ng ³⁷ CI-2,3,7,8-TCDF							
Added							
Total TCDFs							
Total Penta CDFs							
Total Hexa CDFs							
Total Hepta CDFs							
OCDF							

2,3,7,8-TCDD							
3/CI-2,3,7,8-TCDD							
% Recovery							
ng ³⁷ CI-2,3,7,8-TCDD							
Added							
Total Tetra CDDs							
Total Penta CDDs							
124679 & 124689							
H ₆ CDD							
123679 & 123689							
H ₆ CDD							
123469 H ₆ CDD							
123478 H ₆ CDD							
123678 H ₆ CDD							
123467 & 123789							
H ₆ CDD							
Total H ₆ CDDs							
3/CI-123478 H ₇ CDD							
% Recovery							
ng ³⁷ CI-1232478							
H ₇ CDD Added							
1234679 H ₇ CDD							
1234678 H ₇ CDD							
TOTAL H ₇ CDD							
OCDD							
3/CI-OCDD % Recovery							
ng ³⁷ CI-OCDD Added							

DS-65 CROSS SCAN REPORT, RUN: GCNHC0001

* TIC

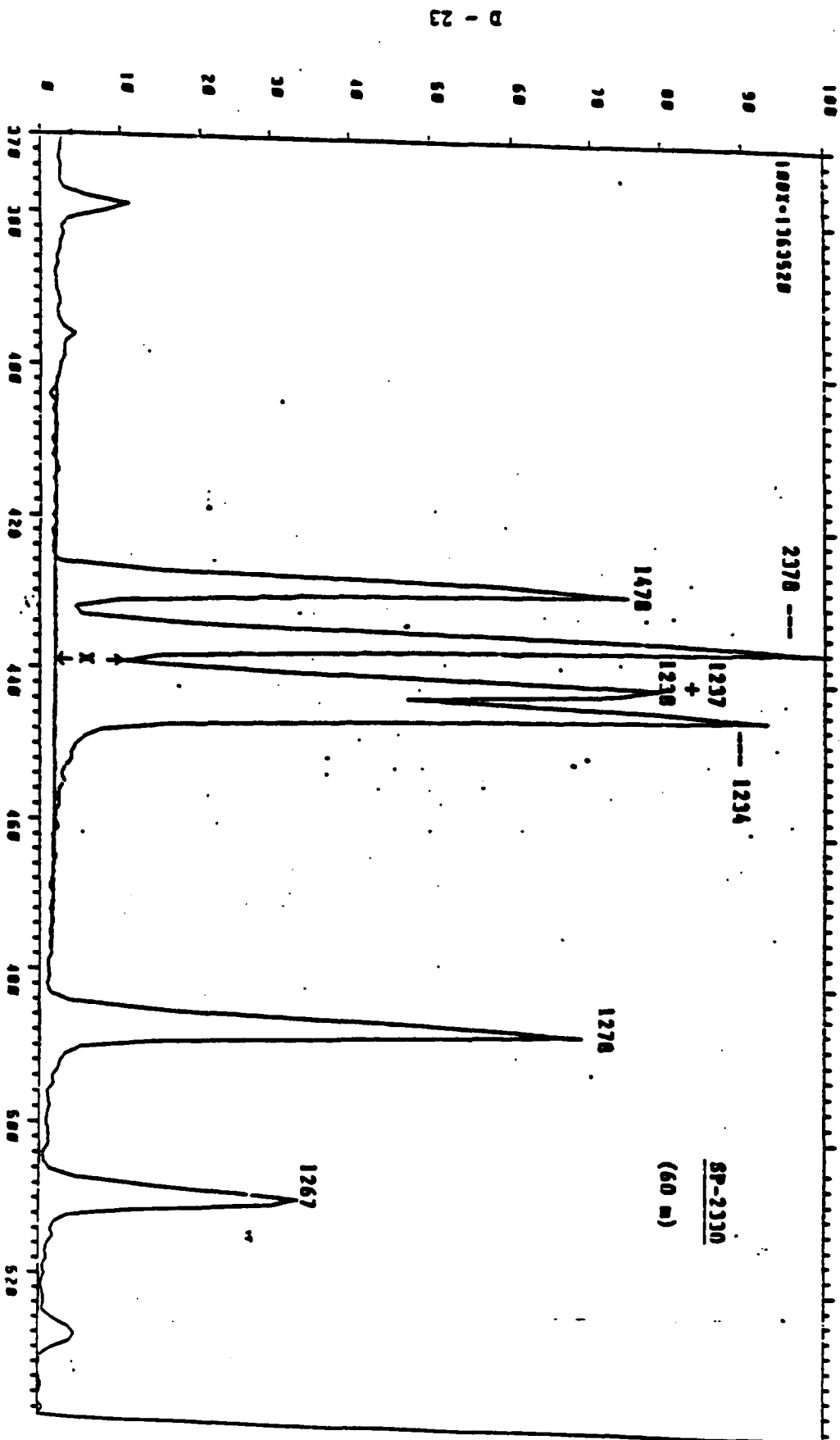


Figure 2. Selected ion current profile for m/z 320 and 322 produced by MS analysis of performance check solution using a 60-m SP-2330 fused silica capillary column and conditions listed in Table I.

DS-55 CROSS SCAN REPORT, RUN: SIL20002

• TIC

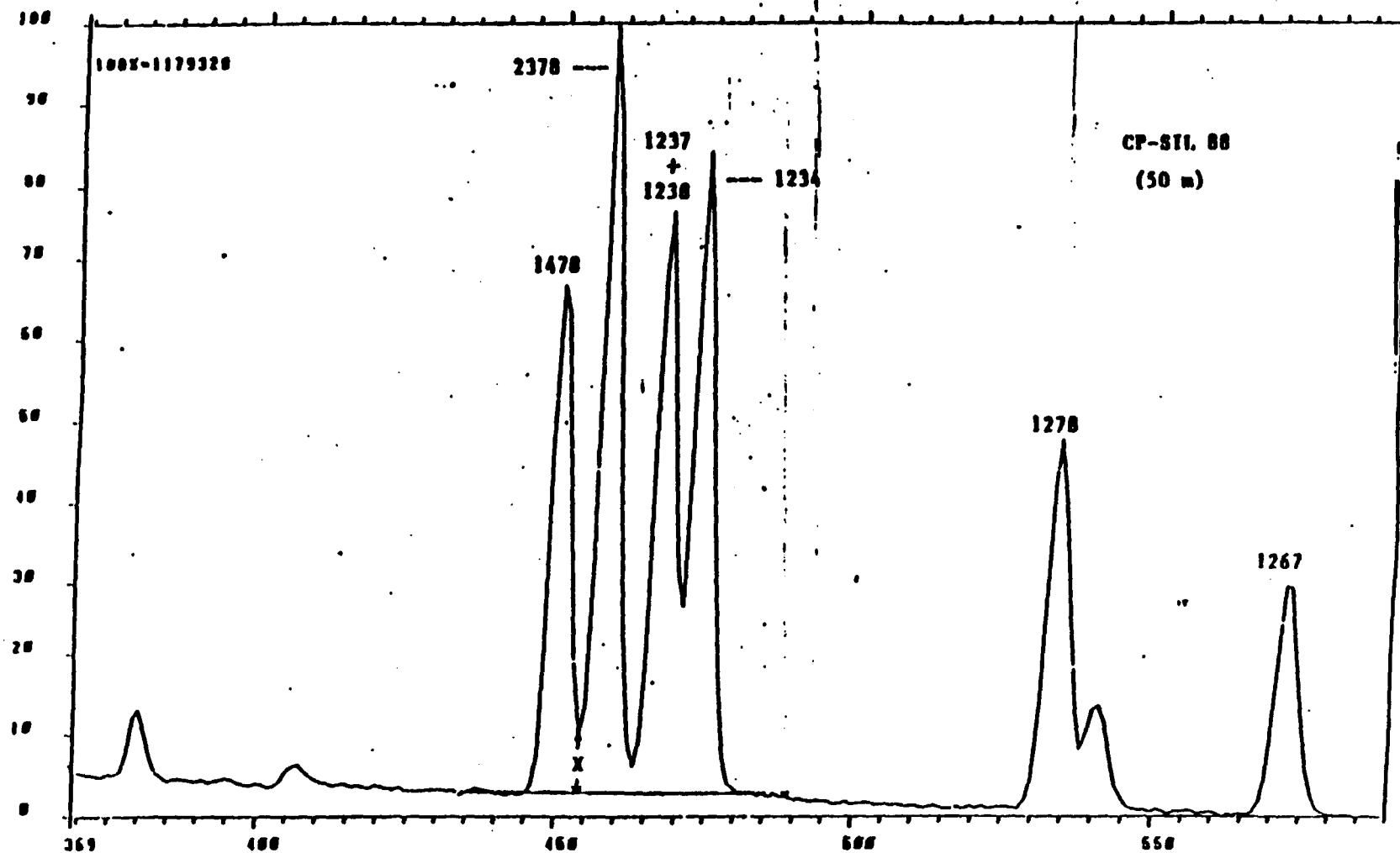


Figure 3. Selected ion current profile for m/z 320 and 322 produced by MS analysis of performance check solution using a 50-m CP-SIL 88 fused silica capillary column and conditions listed in Table 1.

U.S. Environmental Protection Agency
CLP Sample Management Office
P. O. Box 818, Alexandria, Virginia 22313
PHONE: (703)/557-2490 or FTS/557-2490

SAS Number

SPECIAL ANALYTICAL SERVICES
Client Request

☒

Regional Transmittal

☐

Telephone Request

- A. EPA Region/Client: EPA Region V WW Engineering & Science
- B. RSCC Representative: Jan Pels
- C. Telephone Number: 312/ 353-2720
- D. Date of Request: _____
- E. Site Name: Skinner Landfill - West Chester, Ohio

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. General description of analytical service requested: 2, 3, 7, 8 specific tetra-
chlorinated dibenzodioxin and dibenzofuran, total tetra through octa polychlorinated
dibenzodioxins and dibenzofurans, and percent moisture.

2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium, or high concentration):

31 low to medium hazard soil samples containing low levels of dioxins and
furans.

Includes duplicates and blanks.

3. Purpose of analysis (specify whether Superfund (Remedial or Enforcement), RCRA, NPDES, etc.):

Superfund - Remedial Action

4. Estimated date(s) of collection: _____
5. Estimated date(s) and method of shipment: Daily by overnight carrier.
6. Number of days analysis and data required after laboratory receipt of samples:
Laboratory should report results within 45 days.
7. Analytical protocol required (attach copy if other than a protocol currently used in this program):
Extraction: Benzene soxhlet as described in Anal. Chem, 1980, 52, 2045-2054 (Appendix I). Clean-up: HPLC/RPHPLC as described in above reference or Dioxin IFB
WA-86K357 options including carbon column cleanup as needed to meet surrogate percent recovery limits (Appendix II). Instrument: Use HRMS or LRMS to meet target
detection limits.
8. Special technical instruction (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):
1) Determine and report percent moisture (use CLP IFB protocol - Appendix III).
2) Report all data on dry weight basis.
3) Stir soil samples for 30 seconds before removing aliquot.
4) Quantitation and standards requirements (Appendix IV).
5) MUST monitor for the masses of the polychlorinated diphenyl ether interferences
in all furan isomer groups.
9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.): If not completed, format of results will be left to program discretion.
Appendix V for deliverables.
Appendix VI for suggested data report format.
Remember to report percent moisture.
10. Other (use additional sheets or attach supplementary information, as needed):
DO NOT SUBCONTRACT WITHOUT PRIOR REGIONAL APPROVAL.
11. Name of sampling/shipping contact: Bob Phillips
Phone: 616/ 942-9600 EXT 263

I. DATA REQUIREMENTS

<u>Parameter:</u>	<u>Detection Limit</u>	<u>Precision Desired</u> <u>(+/- % or Conc.)</u>
2378 - TCDD/TCDF	5 ppt	
Total TCDD/TCDF	5 ppt	
Total Penta CDD/CDF	20 ppt	
Total Hexa CDD/CDF	20 ppt	
Total Hepta CDD/CDF	20 ppt	
OCDD/OCDF	50 ppt	

II. QC REQUIREMENTS

<u>Audits Required</u>	<u>Frequency of Audits</u>	<u>Limits* (% or Conc.)</u>
Method Blank	1 per 20 SPLS or set	less than Target D.L
In-Lab Matrix Spike		see attachment
Matrix Spike Duplicate		see attachment
Surrogate Spikes	in every sample	

III. ACTION REQUIRED IF LIMITS ARE EXCEEDED:

1) FOLLOW PROCEDURES SPECIFIED IN DIOXIN IFB WA-86K357 (Appendix II).

2) Call Region V if problem persists. Jan Pels 312/ 353-2720 or

Chuck Elly 312/ 353-9087

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for special analytical services. Should you have any question or need any assistance, please call the Sample Management Office.

11. Surrogate, Duplicate and Matrix Spike Limits

A. In Laboratory Matrix Spike

Compound	Level	Recovery Limits
2378-TCDD	< 50 ppt	70 - 130%
2378-TCDF	< 50 ppt	70 - 130%
Penta CDD/CDF	< 200 ppt *	40 - 160%
Hexa CDD/CDF	< 200 ppt *	40 - 160%
Hepta CDD/CDF	< 200 ppt *	40 - 160%
OCDD/OCDF	< 500 ppt *	40 - 160%

* At least one isomer from each of these classes should be used in the spike solution.

B. Surrogate Spikes (required in every sample)

Surrogate	Level ^a	Recovery Limits
³⁷ Cl ₄ 2378-TCDD	5 ng	50 - 115%
¹³ C ₁₂ or ³⁷Cl₄ ^{Pe CDD} 2378-TCDF	5 ng	50 - 115%
³⁷Cl₄ OCDD or ¹³ C ₁₂ -HpCDD	10 - 20 ng	40 - 110%
¹³ C ₁₂ -HxCDD		

^aAdded to 10g sample

C. In Matrix Spike Duplicate

Class	RPD Limit
2378- TCDD/TCDF	< 30% RPD
Penta CDD/CDF	< 60% RPD
Hexa CDD/CDF	< 60% RPD
Hepta CDD/CDF	< 60% RPD
OCDD/OCDF	< 30% RPD

Determination of Tetra-, Hexa-, Hepta-, and Octachlorodibenzo-*p*-dioxin Isomers in Particulate Samples at Parts per Trillion Levels

L. L. Lamparski* and T. J. Nestrick

Analytical Laboratories, 574 Building, Dow Chemical U.S.A., Midland, Michigan 48640

An analytical procedure is presented which permits the isomer-specific determination of tetra-, hexa-, hepta-, and octachlorodibenzo-*p*-dioxins simultaneously at parts per trillion concentrations. Typical data are presented to establish its applicability on a variety of environmental particulate samples. The use of a highly specific sample clean-up procedure based on multiple chromatographies is shown to permit the isomer-specific determination of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2378-TCDD) by packed-column gas chromatography-low-resolution mass spectrometry in the presence of any or all other TCDD isomers.

The determination of parts per trillion (10^{-12} g/g, ppt) concentrations of chemical residues generally requires the use of either highly selective sample purification procedures and/or very specific detectors (1, 2). As detection limits are lowered, the number of possible interferences present at significant concentrations increases dramatically (3). Donaldson (4) has surmised that every known organic chemical could be detected in water at a level of 10^{-10} g/g or higher. Similarly, considering an analysis at the 10 ppt concentration level in a sample matrix that is 99.9% pure, inter- π ions from as many as 10^4 compounds at concentrations 10^4 times higher than the component of interest are possible. Naturally the addition of interferences from sources other than the sample matrix can make this task formidable. Such contamination of laboratory reagents by a multitude of compounds has been reported (5-19). Indeed, in some cases, the controlling factor in determining the limit of detection (LoD) for a given analysis is not the instrumental sensitivity of the detector but the apparent response observed in reagent blanks (20-22).

This paper reports the development of an analytical procedure which permits the isomer-specific determination of 2378-TCDD at low parts per trillion concentrations, even in matrices that have been intentionally fortified with equivalent amounts of each of the other 21 TCDD isomers. Higher chlorinated dioxins, including hexachlorodibenzo-*p*-dioxins (HCDDs, 10 possible isomers), heptachlorodibenzo-*p*-dioxins (H₇CDDs, 2 possible isomers), and octachlorodibenzo-*p*-dioxin (OCDD), can also be determined at low parts per trillion levels by using this technique. In regards to the isomer-specific determination of 2378-TCDD, the other 21 TCDD isomers may also be considered as possible interferences. Several publications have recently appeared which demonstrate CDD determination capabilities but do not provide complete TCDD isomer specificity (23-32).

EXPERIMENTAL SECTION

Reagents. The preparation of 44% concentrated sulfuric acid on silica, 10% silver nitrate on silica, basic alumina, and purified nitrogen (FemtoGas) have been described (1).

Silica. This adsorbent is prepared from chromatographic grade silicic acid as described for the preparation of 44% sulfuric acid on silica (1).

12% 1 M Sodium Hydroxide on Silica. The silica support is prepared as described (1). Activated silica is weighed into an appropriately sized glass bottle. On the basis of the support

weight, the amount of 1 M aqueous sodium hydroxide necessary to yield a reagent containing 33% by weight is added in a stepwise fashion with shaking to produce a uniformly coated, free-flowing powder.

Chemicals and Solvents. All solvents used are Burdick and Jackson, distilled-in-glass quality. Laboratory chemicals (H_2SO_4 , $AgNO_3$, $NaOH$) are ACS reagent grade. These materials are tested by subjecting them to the analytical procedure to verify the absence of contamination. Spectrophotometric grade Gold-label *n*-hexadecane was obtained from Aldrich Chemical Co. (Milwaukee, WI) and was purified by passage through basic alumina.

Expendables. Pyrex glass wool, silica boiling stones, and disposable pipettes are cleaned before use. Glass wool and boiling stones are Soxhlet extracted ~1 h consecutively with the following solvents: methanol, chloroform + benzene (1:1 by volume), benzene, and methylene chloride. They are then dried in a hot air oven at ~160 °C for ~1 h. Disposable pipettes are cleaned ultrasonically in deionized water and then methanol and finally methylene chloride prior to drying at ~160 °C. Final sample residues are stored in React-Vials obtained from Pierce Chemical Co. (Rockford, IL). The vials are cleaned by washing with detergent and water and then boiled sequentially in benzene + chloroform + methanol (1:1:1 by volume), benzene + chloroform (1:1 by volume), benzene, and finally methylene chloride. They are air-dried and again rinsed with methylene chloride immediately before use.

Dioxin Standards. The primary standard of 2378-TCDD was prepared by W. W. Muelder (Dow Chemical Co.) and its structure was confirmed by single-crystal X-ray diffraction techniques (33). Purity was assessed at 98% by mass spectrometry. Standards of other TCDD isomers were synthesized and isolated as previously described (34). Primary standards of 1,2,3,4,6,7,8-heptachlorodibenzo-*p*-dioxin (1234678-H₇CDD) and OCDD were synthesized by H. G. Fraaije and W. W. Muelder (Dow Chemical Co.). A standard containing two HCDD isomers was prepared by Aniline (35). Standards of 1234678-H₇CDD and the 10 HCDD isomers were synthesized and isolated in a manner similar to that reported for TCDDs (34). Isotope-enriched ^{14}C -2378-TCDD and ^{14}C -123478-HCDD were synthesized by A. S. Kende (University of Rochester, Rochester, NY). Mass spectrometric analysis indicated these standards to be 86 atom % and 43 atom % ^{14}C , respectively. Perchlorination of the ^{14}C -2378-TCDD provided ^{14}C -OCDD.

Apparatus. **Reverse-Phase High-Performance Liquid Chromatography (RP-HPLC).** Residues containing chlorinated dioxins are injected into the RP-HPLC system: column, two 6.2 x 250 mm Zorbax-ODS (DuPont Instruments Division, Wilmington, DE) columns in series; isocratic eluent, methanol at 2.0 mL/min; pump, Altex Model 110A; column temperature, 50 °C; UV detector, Perkin-Elmer Model LC-45T liquid chromatographic column oven and detector operated at 0.02 au/s at 235 nm; injector, Rheodyne Model 7120 with 50- μ L sample loop.

Normal-Phase Adsorption High-Performance Liquid Chromatography (Silica-HPLC). Residues containing TCDDs are injected into the silica-HPLC system: column, two 6.2 x 250 mm Zorbax-SIL (DuPont Instruments Division) columns in series; isocratic eluent, hexane at 2.0 mL/min; pump, Altex Model 110A; column temperature, ambient; UV detector, Laboratory Data Control Model 1204 variable-wavelength detector at 0.05 au/s at 235 nm; injector, Rheodyne Model 7120 with 100- μ L sample injection loop. The columns were activated by the procedure of Brodeur et al. (36).

Packed-Column Gas Chromatography-Low-Resolution Mass Spectrometry (GC-LRMS). Chlorinated dioxin quantification

was accomplished by GC-MS using a Hewlett-Packard Model 5992-A operating in the selected ion mode (SIM) at unit resolution; column, 2 mm i.d. \times 310 cm silylated glass; packing, 0.60% OV-17 silicone + 0.40% Poly S-179 on 80/100 mesh Permabond Methyl Silicone-10 cycle (HNU Systems Inc., Newton, MA); injection port temperature, 230 °C on-column; carrier gas, helium at 14 cm³/min; separator, single stage glass jet operating at column temperature; electron energy, 70 eV. TCDD analyses conditions: column temperature, 246 °C isothermal; ions monitored, native TCDDs at m/e 320, 322, and 324, and ¹³C-2378-TCDD internal standard at m/e 332. Higher chlorinated dioxin analyses conditions: column temperature, programmed from 230 to 300 °C at 10 °C/min and hold at maximum; ions monitored, native HCDDs at m/e 388, 390, and 392, native H₂CDDs at m/e 422, 424, and 426, and native OCDD at m/e 458, 460, and 462. ¹³C-123478-HCDD and ¹³C-OCDD are monitored at m/e 398 and 470, respectively.

Environmental Particulate Samples. Industrial Dust. Particulates were removed from the air intake filtration system from a research building located in Midland, MI.

Electrostatically Precipitated Fly Ash. Particulates were collected from the ash-removal system associated with the electrostatic precipitator on the Nashville Thermal Transfer Corp. refuse incinerator located in Nashville, TN.

Activated Municipal Sludge. Representative samples were removed from the center of a commercially purchased 20-kg bag of Milwaukee Milorganite.

Urban Particulate Matter. Standard Reference Material No. 1648 was obtained from the National Bureau of Standards (NBS).

European Fly Ash. Particulate emissions from a municipal trash incinerator were collected on filter paper by a nonisokinetic sampling procedure. The location of the sampling port was downstream from the electrostatic precipitator. This incinerator was not operated to recover energy for power generation.

Sample Preparation. Prior to GC-MS SIM quantification, the sample is prepared by using five basic steps: (1) chlorinated dioxins removal from the matrix via hydrocarbon extraction, (2) chemically modified adsorbent treatment of the extract to remove easily oxidizable species, (3) adsorbent treatment to remove common chemical interferences, (4) RP-HPLC residue fractionation to remove residual chemically similar interferences and to separate dioxins present into groups according to their degree of chlorination, and (5) silica-HPLC refractionation of the RP-HPLC TCDD fractions to provide a second high-efficiency chromatographic separation having different selectivity to remove residual interferences and to permit TCDD isomer specificity.

An appropriately sized all-glass Soxhlet extraction apparatus equipped with a water-cooled condenser, a 43 \times 125 mm glass thimble with coarse frit, a 250-mL boiling flask, and a temperature-controlled heating mantle is assembled. Each of the parts is thoroughly scrubbed with an aqueous detergent solution, rinsed with deionized water followed by acetone, methanol, and methylene chloride, and finally air-dried. Depending on the particulate sample size (larger samples require most), 5–15 g of silica is charged into the thimble followed by a plug of glass wool large enough to cover the silica bed completely. The assembled system (thimble installed) is charged with benzene (~250 mL) and allowed to reflux at a recycle rate of ~20 mL/min for a minimum period of 2 h. Following this preextraction period, the system is permitted to cool and the total benzene extract is discarded. The extraction thimble is removed and allowed to drain completely on a clean wire stand in a fume hood. The glass wool plug is removed with clean forceps while a representative particulate sample, ranging from 50 mg for filtered airborne particulates to 100 g for heavy soils, is quickly charged on top of the silica bed. The glass wool plug is replaced and the thimble returned to the Soxhlet extractor body. At this time aliquots of isotopically labeled 2378-TCDD, 123478-HCDD, and OCDD are introduced directly into the particulate bed. The system is recharged with fresh benzene and exhaustively extracted at the rate previously described for a minimum period of 16 h. Each sample or set should have at least one system treated as described for the sample to serve as a reagent blank.

Upon completion of the prescribed extraction period, the flask containing the benzene extract is removed and fitted with a three-

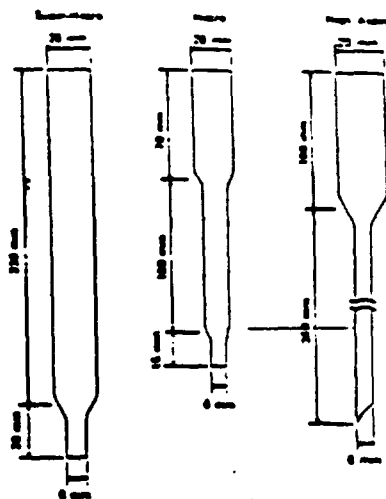


Figure 1. Liquid chromatographic clean-up columns.

to six-stage Snyder distillation column. The volume of the extract solution is then reduced by atmospheric pressure distillation of the benzene solvent to a final volume of approximately 25 mL. The concentrated benzene extract is then diluted with a roughly equal volume of hexane when cool.

Bulk matrix (benzene extractables other than CDDs) removal is accomplished by passing the residue extract solution through a Super-Macro chromatographic column (see Figure 1) prepared as follows. The column is thoroughly washed and dried just prior to use via the same procedure described for the Soxhlet extractor. A glass wool plug is inserted into the end of the column to serve as a bed support, and the following reagents are then carefully weighed directly into the column: 1.0 g of silica (bottom layer), 2.0 g of 33% 1 M sodium hydroxide on silica, 1.0 g of silica, 4.0 g of 44% concentrated sulfuric acid on silica, and 2.0 g of silica (top layer). The freshly packed column is then immediately prewashed with 30 mL of hexane and the effluent discarded. The residue extract is then passed through the column followed by 8 \times 5-mL hexane rinses of the boiling flask vessel. Following these rinses an additional 30 mL of hexane is passed through the column. The total effluent is collected in a 150-mL beaker and then evaporated to dryness under a stream of Fentogas nitrogen. A single drop of *n*-hexadecane (~25 mg) is added to the reagent blank prior to its evaporation to dryness as a means of improving internal standard recovery.

Common chemical interferences are removed by passage of the residue through a dual column system consisting of a top Macro chromatographic column draining into a bottom High Aspect column. (See Figure 1.) Each of these columns is cleaned as previously described and a glass wool bed support inserted just prior to use. The Macro column is packed with 1.5 g of 10% silver nitrate on silica and prewashed with 15 mL of hexane prior to use. The High Aspect column is packed with 5.0 g of basic alumina. When the top Macro column prewash has drained, it is positioned over the High Aspect column reservoir. The sample residue is dissolved in ~15 mL of hexane and introduced into the top column followed by 3 \times 5-mL hexane beaker rinses. Following the rinses, an additional 30 mL of hexane is passed through the system. When drained, the top column is discarded. After the hexane has drained to bed level in the High Aspect column, 50 mL of 50% (v/v) carbon tetrachloride in hexane is passed through. The total effluent to this point can be discarded. A 25-mL glass vial (cleaned same as chromatographic columns) is used to collect the total effluent after 22.5 mL of 50% (v/v) methylene chloride in hexane is introduced into the column. When elution is complete this fraction which contains chlorinated dioxins is evaporated to dryness under a stream of Fentogas nitrogen (1).

RP-HPLC fractionation of the residue is initiated by calibration of the appropriate collection zones for TCDDs, HCDDs, H₂CDDs, and OCDD.

Table I. TCDD Isomer RP-HPLC Fractionation Scheme and Specific Retention Indices

TCDD isomer	RP-HPLC abs RT, ^a min	silica- HPLC rel RT ^b	GC packed column rel RT ^c
RP-Iso No. 1 Fraction			
1269	11.6-13.0	1.702	0.996
1469	11.6-13.0	1.497	0.912
1267/1259	12.2-12.9	1.623	1.081
	12.2-12.9	1.795	1.200
1268/1279	13.3-13.9	1.238	0.986
	13.3-13.9	1.291	1.063
1369/1478	13.3-13.9	1.220	0.802
	13.3-13.9	1.340	0.907
RP-2378 Fraction			
1246/1249	13.7-14.5	1.325	0.896
	13.7-14.5	1.411	0.898
2378	13.8-14.5	1.000	1.006 ^d
1236/1239	13.8-14.4	1.356	1.037
	14.4-15.2	1.350	0.969
1278	14.0-14.7	1.288	0.893
1237/1238	14.0-15.0	1.100	0.879
	14.0-15.0	1.128	0.990
1247/1248	14.2-15.1	1.154	0.854
	14.2-15.1	1.189	0.887
RP-Iso No. 2 Fraction			
1378	14.9-15.7	1.000	0.858
1379	14.9-15.9	0.940	0.771
1368	15.9-16.8	0.977	0.729
1234	15.8-16.8	1.248	0.960

^a RP-HPLC abs RT = absolute retention time (± 0.1 min) to collect peak. ^b Silica-HPLC rel RT = retention time relative to 2378-TCDD (± 0.010). ^c GC-packed column rel RT = retention time relative to ¹⁴C-2378-TCDD (± 0.005). ^d Native 2378-TCDD elutes slightly later than ¹⁴C-2378-TCDD.

subjected to reverse-phase high-performance liquid chromatography fractionation. The resultant liquid chromatograms monitored by a UV detector at 235 nm ($\sim \lambda_{\text{max}}$ for TCDDs) and 0.02 a.u. are shown in Figure 3b-e. Shown in Figure 3a is the chromatogram obtained for a CDD calibration standard by RP-HPLC. Although the appropriate CDD collection zones, denoted by dotted lines, were initially established by individual injections of 22 TCDD isomers, 10 HCDD isomers, 2 H₂CDD isomers, and OCDD, we routinely compute their location from the observed retention times of only a few selected species. The specific RP-HPLC retention indices for TCDDs are given in Table I and those for HCDDs, H₂CDDs, and OCDD are listed in Table II.

As indicated, all 22 TCDD isomers can be fractionated from a sample residue by collecting the column effluent beginning at ~ 11.5 and ending at ~ 17.0 min. The initial stage of TCDD isomer specificity is achieved by collecting the 22 isomers in three separate fractions as shown. TCDD Iso No. 1 (RP-HPLC TCDD isomer fraction no. 1) can contain the following isomers: 1269-, 1469-, 1267-, 1259-, 1268-, 1279-, 1369-, and 1478-TCDD. The TCDD 2378 fraction contains 1246-, 1249-, 2378-, 1236-, 1239-, 1278-, 1237-, 1238-, 1247-, and 1248-TCDD. TCDD Iso No. 2 contains the remaining four isomers: 1378-, 1379-, 1368-, and 1234-TCDD. Preliminary evidence, gained by fortifying samples with roughly equal amounts of all 22 TCDD isomers at approximately the 150 ppt concentration level, has indicated that three of the possible isomers in TCDD Iso No. 1 must be sacrificed in order to ensure quantitative collection of 2378-TCDD in the following fraction. This consequence will be discussed later. Its occurrence is related to the RP-HPLC retention times for the isomers: 1369-TCDD, 1478-TCDD, and one of the pair 1268- or 1279-TCDD having SI rel RT 1.238 (normal-phase silica HPLC retention time

Table II. HCDDs, H₂CDDs, and OCDD Retention Indices

CDD isomer	silica- HPLC rel RT ^a	RP- HPLC abs RT ^b	GC-packed column rel RT ^c
HCDDs:			
123469-HCDD	1.081	19.23	0.954
123467-HCDD	1.192	19.47	1.077
124679/124689-HCDD	0.958	19.62	0.805
124679/124689-HCDD	0.972	19.70	0.806
123678/123789-HCDD	1.080	20.07	1.103
123679/123689-HCDD	0.970	20.20	0.903
123679/123689-HCDD	1.039	20.23	0.908
123678/123789-HCDD	0.974	20.85	1.016
123478-HCDD	0.941	21.02	1.006 ^d
123468-HCDD	0.990	21.87	0.861
H ₂ CDDs:			
1234679-H ₂ CDD		24.00	
1234678-H ₂ CDD		24.65	
OCDD			
		29.40	

^a Silica-HPLC rel RT = retention time relative to 2378-TCDD (± 0.010). ^b RP-HPLC abs RT = absolute retention (± 0.1 min) at peak maximum. ^c GC packed column rel RT = retention time relative to ¹⁴C-123478-HCDD. ^d Native 123478-HCDD elutes slightly later than ¹⁴C-123478-HCDD.

relative to 2378-TCDD). Their retention times are very close to the fraction boundary separating Iso No. 1 and 2378 and are split rather irreproducibly between these fractions. Although these isomers do not necessarily interfere with the quantitation of the isomers expected to the present in the TCDD 2378 fraction, their quantitation essentially become impossible. For cases where quantitation of these three TCDDs is required, a second aliquot of sample residue can be fractionated by RP-HPLC in such a manner so as to expand the Iso No. 1 fraction to ensure their collection.

The 10 HCDD isomers are collected in accordance with Figure 3 and Table II. Although isomer-specific HCDD determinations are possible by using essentially the same chromatography procedures described for TCDDs (i.e., RP-HPLC — silica-HPLC — GC), we have not yet applied this system to samples. Similarly, the two H₂CDD isomers are collected in a single fraction, as is OCDD.

The RP-HPLC residue fractionation chromatograms in Figure 3 are typical of those associated with particulate samples. The presence of higher chlorinated species, such as H₂CDDs and OCDD, can often be observed at this point in the analysis. Although the UV detector has been adjusted for maximum sensitivity for TCDDs, under these conditions a detectable response for HCDDs, H₂CDDs, and OCDD is obtained for approximately 5 ng. Similarly, heptachlorodibenzofurans (H₇CDFs) and octachlorodibenzofuran (OCDF) may also be observed in the RP-HPLC fractionation. Because of the lack of availability of authenticated chlorinated dibenzofuran (CDFs) standards, we have made no attempt to quantitate these species. Via collection of appropriate RP-HPLC fractions, and capillary GC-EC and GC-LRMS, we have established the possible presence of four H₇CDF isomers and OCDF in a variety of particulate samples.

Refractionation of the RP-HPLC TCDD fractions via normal-phase HPLC (silica-HPLC) is the final stage of the sample cleanup prior to GC-LRMS analysis. Normal monitoring of these chromatograms with a UV detector at 0.1 a.u. and 235 nm does not produce observable peaks with the exception of the ¹⁴C-2378-TCDD internal standard. For this reason example chromatograms are omitted. Table I lists the individual TCDD isomers contained in each RP-HPLC TCDD fraction. Included are the RP-HPLC, silica-HPLC, and GC packed column retention indices for each species. By use of

standard containing approximately 10–20 ng each: 2378-TCDD, HCDD(s), H₂CDD(s), and OCDD in no more than 30 μ L of chloroform. In accordance with the chromatogram obtained, appropriate collection zones are established for each of these species (see Discussion section). Following calibration, the injector is rinsed with copious quantities of chloroform, to include multiple consecutive injections of 50 μ L of chloroform into the column to ensure that no residual chlorinated dioxins remain.

The residue is prepared for RP-HPLC fractionation by quantitative transfer to a 0.3-mL Reacti-Vial. Quantitative injection requires complete residue solubility in 30 μ L or less of chloroform. Larger injections of chloroform into this RP-HPLC system severely reduce column efficiency. An aliquot of no more than 30 μ L can be fractionated if the sample residue requires greater amounts of chloroform to be dissolved. Appropriate chlorinated dioxin fractions are collected in 25-mL volumetric flasks, equipped with ground glass stoppers, containing ~1 mL of hexane. The chlorinated dioxins are recovered by addition of 2% (w/v) aqueous sodium bicarbonate. The hexane layer is transferred to a 5-mL glass vial and the aqueous phase is extracted three additional times with ~1 mL of hexane. The combined extracts are then evaporated to dryness under a stream of Pentos nitrogen. HCDD, H₂CDD, and OCDD fractions are quantitatively transferred to 0.3-mL Reacti-Vials and diluted to appropriate volumes for determination by GC-LRMS.

Regarding the case for an isomer-specific 2378-TCDD determination, additional silica-HPLC fractionation of the RP-HPLC 2378-TCDD fraction is required (see Discussion section). Calibration of the appropriate collection zone is accomplished by injecting approximately 10 ng of 2378-TCDD into the silica-HPLC in 60–80 μ L of hexane and monitoring the chromatogram obtained. Adequate isomer specificity is obtained when the silica-HPLC columns are sufficiently dry so as to provide a 2378-TCDD retention time ranging from a minimum of 12.5 min to maximum of 17 min (24). Following injection of the residue fraction, the chromatogram is monitored and the appropriate 2378-TCDD fraction is collected in a 5-mL glass vial. This fraction is then evaporated to dryness under a stream of Pentos nitrogen and diluted to appropriate volumes for determination by GC-LRMS. This procedure can also be used to collect other TCDD isomers as described in the Discussion section; see Figure 2.

DISCUSSION

The purpose of this paper is to demonstrate the feasibility of using a single multiple-step procedure to accomplish the isomer-specific determination of TCDDs, HCDDs, H₂CDDs, and OCDD at low part per trillion concentrations in a variety of environmental particulate samples. There were two prerequisites for our development of the methodology. First, the sample cleanup must be capable of recovering each of the listed chlorinated dioxin (CDD) groups from a single sample and from a single workup. And second, all procedures must use the least sophisticated and most reliable instrumentation possible so that such analyses could be conducted in the greatest number of analytical facilities. These prerequisites have determined the means by which the described analyses can be accomplished. That is, a neutral or acid extraction procedure must be used. Any treatment of either the sample or its extracts with strong bases is known to cause degradation of the higher chlorinated dioxins (21, 37). In accordance with ease of handling and the general solubility characteristics of higher chlorinated dioxins (least soluble species), continuous benzene extraction was found to be adequate for all particulate samples examined. The selection of packed-column gas chromatography-low-resolution mass spectrometry as opposed to capillary column gas chromatography-high-resolution mass spectrometry represents our attempt to use the least sophisticated instrumentation for CDD determination. Because packed-column GC-LRMS is inherently more subject to possible interference than capillary column GC-HRMS, a more rigorous sample preparation is required. The approach of combining classical extraction and adsorbent clean-up techniques with consecutive RP-HPLC and silica-HPLC residue

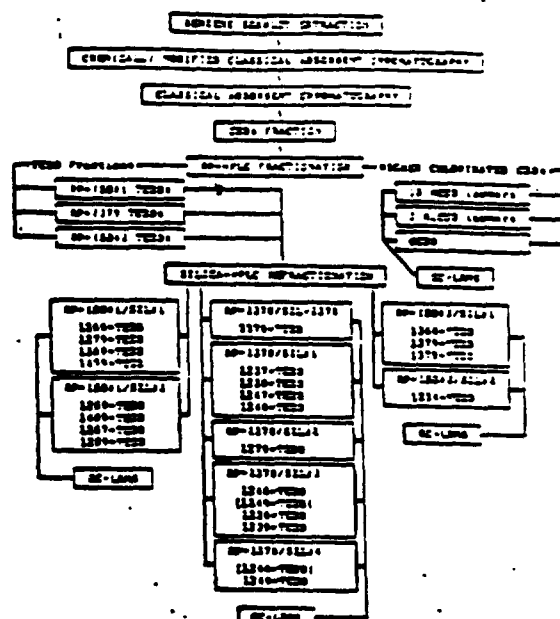


Figure 2. Block diagram for CDD sample preparation.

fractionations can be one solution to this problem. Under these circumstances a significant portion of the method capability to prevent MS interferences during the identification and quantification of CDDs is relegated to the cleanup rather than to the final gas chromatographic separation. This can be advantageous when dealing with highly contaminated samples because the chromatographic capacity of the clean-up steps is usually much greater than that of the GC column, especially when capillaries are used. In addition, this approach incorporates the consecutive RP-HPLC and silica-HPLC steps that we have published for the separation and isolation of the 22 TCDD isomers (34). Their described application in this procedure permits the analyst to predetermine which possible TCDD isomers can be present in a given residue fraction. Hence, the necessity of using a capillary GC column to obtain improved TCDD isomer separations is eliminated. This capability may be of utmost importance as the authors are not aware of any published data suggesting that all 22 TCDD isomers can be separated simultaneously using a single capillary GC column. The described methodology will address this problem.

It is to be understood that this procedure has been developed and used for survey purposes on a variety of different environmental particulates. A complete method validation including controls, fortifications, and replicates would be required for each specific matrix before its absolute degree of reliability can be established. The inclusion of isotopically enriched TCDD, HCDD, and OCDD internal standards provide a reasonable degree of reliability under the circumstances of its described uses.

The samples 1.0 g of NBS urban particulate matter, 1.0 g of industrial dust, 1.0 g of electrostatically precipitated fly ash from a municipal burner (fly ash), 1.67 g of Millorganite, and 0.3968 g of European flyash were Soxhlet extracted with benzene for ~16 h and the resulting residues processed through the preliminary liquid chromatographic clean-up steps. Each sample, to include a reagent blank, was fortified with 5–20 ng of isotopically enriched internal standard CDDs (¹⁴C enrichment) prior to analysis. After transfer to a 0.3-mL Reacti-Vial and evaporation of the solvent, all samples yielded a visible white residue. Each of these was then quantitatively

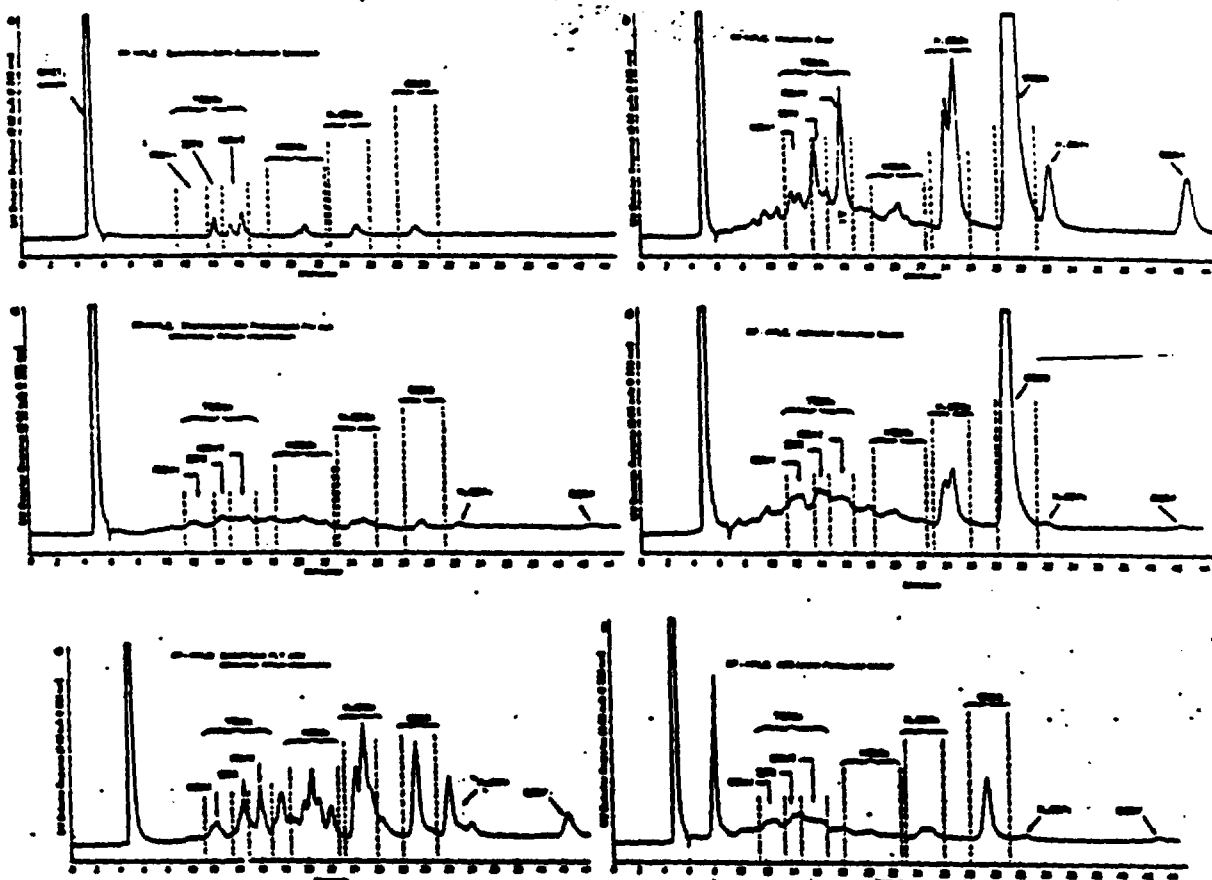


Figure 2. RP-HPLC fractionation chromatograms: (a) calibration standard, (b) industrial dust, (c) electrostatic fly ash, (d) municipal sludge, (e) European fly ash, (f) NBS urban particulates.

this information, appropriate fractions can be collected from the silica-HPLC which permit isomer-specific GC-LRMS identification and quantitation.

The silica-HPLC TCDDs fractionation scheme in Table III is designed to provide maximum isomer-specific information when using our packed-column GC-LRMS analysis, while minimizing the total number of fractions collected. Remembering that the primary goal was to provide the highest quality analytical data for 2378-TCDD, this scheme is adequate. Examination of the GC packed column relative retention times (GC rel RT, TCDD retention time relative to ^{14}C -2378-TCDD) for all TCDDs present in the RP-2378-TCDD fraction indicates that four other TCDDs have GC rel RTs within ± 0.080 (~ 12 s for 4 min absolute retention time for ^{14}C -2378-TCDD) of 2378-TCDD. Arbitrarily defining GC rel RT ± 0.080 as the minimum GC packed column separation for qualitative identification of a TCDD isomer from 2378-TCDD and then direct GC-LRMS analysis of the RP-2378-TCDD fraction would yield a 2378-TCDD value which could include a maximum of four other TCDD isomers (2378-TCDD + 4). However, examination of the silica HPLC relative retention times (Sil rel RT, TCDD retention time relative to 2378-TCDD) for these TCDDs indicates that 2378-TCDD is the first isomer to elute. The next isomer to elute is 1237/1238-TCDD (Sil rel RT 1.10); however, even at the minimum acceptable silica-HPLC retention time for 2378-TCDD which is ~ 12.5 min, this isomer is separated by ~ 1.73 min. The remaining nine TCDD isomers, other than 2378-TCDD, present in the RP-2378-TCDD fraction can be determined as single isomers with the exception of those in Sil Fraction No. 1. Although 1237-

1238-, 1247-, and 1248-TCDD are essentially baseline separated by silica-HPLC, attempts to collect them in individual fractions under conditions where the species cannot be observed by a UV detector would be difficult. Hence a single fraction is collected for GC-LRMS analysis. As indicated by the respective GC rel RTs, these isomers can be determined as a total for 1237- and 1238-TCDD and a total for 1247- and 1248-TCDD.

Three of the TCDD isomers present in RP-fac No. 1 are sacrificed in order to ensure maximum recovery of 2378-TCDD in the following RP-HPLC fraction. The consequence of this situation is the possible presence of 1268/1279-TCDD (Sil rel RT 1.238), 1369-TCDD, and 1478-TCDD in the RP-2378-TCDD fraction. Regarding their effect upon the isomer-specific determination of 2378-TCDD, it can be observed that no interferences occur by virtue of both their respective silica-HPLC rel RTs and their GC-packed column rel RTs. However, under circumstances where the 1268/1279-TCDD (Sil rel RT 1.238) isomer is relatively high in concentration, it could be misidentified as 1237- and 1238-TCDD present in Sil Fraction No. 1 of the RP-2378-TCDD fraction. This interference results from similar GC rel RTs for these isomers as indicated in Table III. The 1369/1478-TCDD (Sil rel RT 1.220) will not cause any similar interference problems with these TCDDs present in RP-2378-TCDD fraction—Sil Fraction No. 1 because of its GC rel RT of 0.902. The remaining isomer, 1369/1478-TCDD (Sil rel RT 1.340), if present in high concentration may interfere with 1246/1249-TCDD (Sil rel RT 1.411) in RP-2378-TCDD fraction—Sil Fraction No. 3.

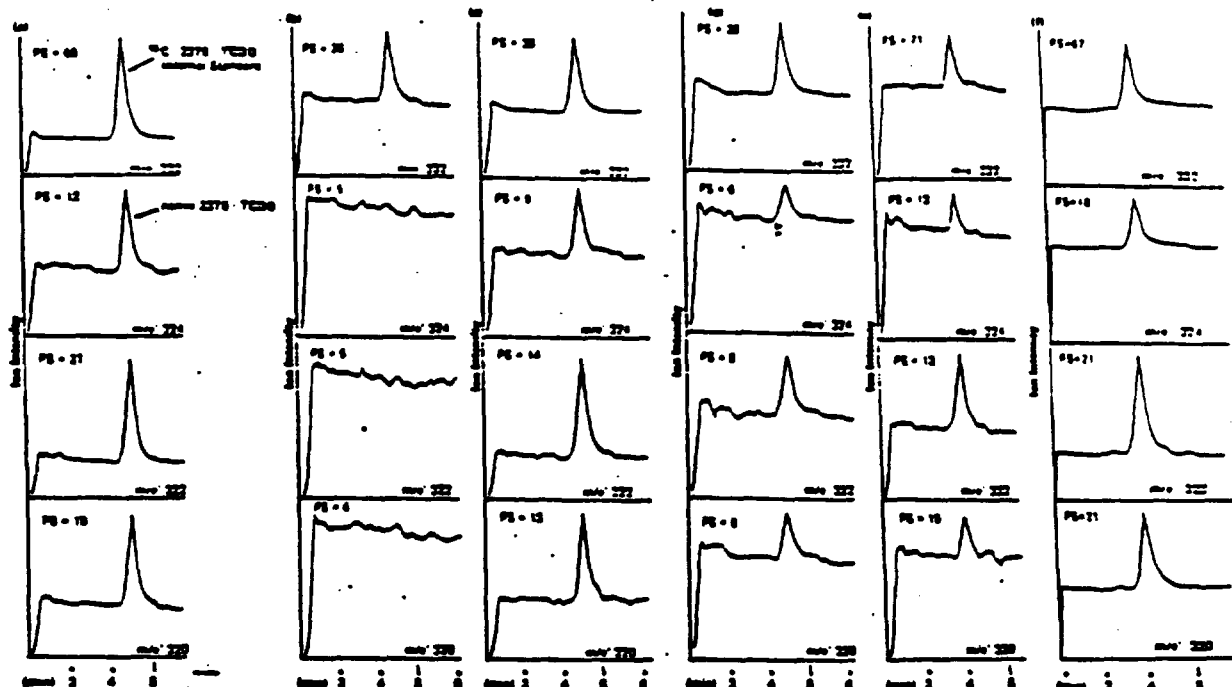


Figure 4. Isomer-specific 2378-TCDD GC-LRMS mass chromatograms: (a) calibration standard, (b) reagent blank, (c) industrial dust, (d) electrostatic fly ash, (e) municipal sludge, (f) European fly ash.

GC-LRMS mass chromatograms for the isomer-specific 2378-TCDD fractions of each particulate sample analyzed are shown in Figure 4. Native 2378-TCDD is monitored at m/e 320, 322, and 324 and ^{13}C -2378-TCDD at 332. The calibration standard (Figure 4a shows a typical for a 2- μ L injection of a reference standard containing 100 pg/ μ L of native 2378-TCDD and 500 pg/ μ L of ^{13}C -2378-TCDD.

The GC-LRMS mass chromatograms in Figure 5 compare the analysis of the RP-2378-TCDD fraction from electrostatically precipitated fly ash for 2378-TCDD, before and after silica-HPLC refractionation. As a means of ensuring homogeneity, a 2-g portion of sample was processed through the cleanup including RP-HPLC fractionation. At this point the RP-2378-TCDD fraction was divided into two equal portions, each equivalent to 1 g of original sample. One portion was analyzed directly by GC-LRMS as illustrated in Figure 5a. The other portion was further fractionated by silica-HPLC, the S11 Fraction 2378 collected, and this residue analyzed by GC-LRMS (Figure 5b). Comparison of 2378-TCDD quantitation for these residues yields 1500 ppt before silica-HPLC refractionation, and 430 ppt after. The value obtained before silica-HPLC refractionation must be qualified as being the concentration of 2378-HPLC plus four possible unseparated isomers (see Table IV).

Isomer-specific TCDD analysis data for each of the described particulate samples appear in Tables IV and V. Quantitation of TCDDs was accomplished by averaging the observed response at m/e 320, 322, and 324 for all cases except where denoted. Instrumental calibration for all TCDD isomers was based upon the observed responses for a primary standard of 2378-TCDD. The listed concentrations for 2378-TCDD have been corrected for recovery of the ^{13}C -2378-TCDD internal standard as given in Table V. Concentrations given for all other TCDD isomers represent absolute observed values. The limit of detection (LoD) for all species was defined as $2.5 \times$ peak-to-valley noise in a region nearby the expected elution time. Observed concentrations less than the LoD are listed as not detected (ND).

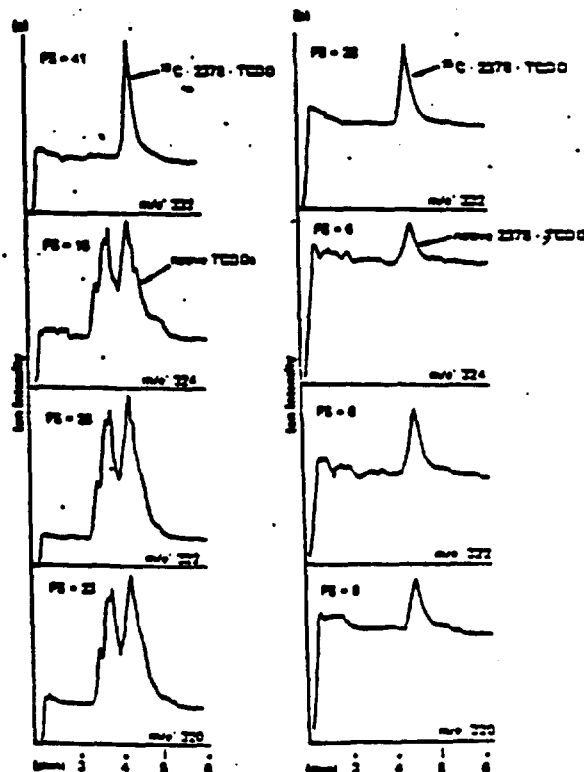


Figure 5. Comparative 2378-TCDD GC-LRMS mass chromatograms for electrostatic fly ash (a) after RP-HPLC (RP-2378 fraction) (b) after silica-HPLC (silica-2378 fraction).

As a means of investigating the degree of reliability associated with the isomer-specific determination of 2378-TCDD in a sample containing equivalent concentrations of all 21 other

Table III. TCDD Isomer Silica-HPLC Fractionation Scheme and Specific Retention Indices

TCDD isomer	silica-HPLC rel RT ^a	Sil collection zone rel RT ^a	GC packed column rel RT ^a
RP-Isol No. 1 Fraction TCDDs			
Sil fraction no. 1		1.180-1.370	
1268/1279-TCDD	1.238 ^b		0.956
	1.291		1.063
1369/1478-TCDD	1.220 ^c		0.802
	1.340 ^c		0.907
Sil fraction no. 2		1.455-1.850	
1269-TCDD	1.702		0.998
1469-TCDD	1.497		0.912
1267/1239-TCDD	1.823		1.081
	1.795		1.200
RP-2378 Fraction TCDDs			
Sil fraction 2378		0.950-1.050	
2378-TCDD	1.000		1.006 ^d
Sil fraction no. 1		1.050-1.244	
1237/1238-TCDD ^e	1.100		0.979
	1.128		0.990
1247/1248-TCDD ^e	1.154		0.854
	1.199		0.867
Sil fraction no. 2		1.244-1.300	
1278-TCDD	1.288		0.893
Sil fraction no. 3		1.300-1.385	
1246/1249-TCDD	1.328		0.896
1236/1239-TCDD	1.356		1.037
	1.380		0.968
Sil fraction no. 4		1.385-1.450	
1246/1249-TCDD	1.411		0.898
RP-Isol No. 2 Fraction TCDDs			
Sil fraction no. 1 ^f		0.900-1.050	
1368-TCDD	0.940		0.729
1379-TCDD	0.977		0.771
1378-TCDD	1.000		0.858
Sil fraction no. 2 ^f		1.210-1.288	
1234-TCDD	1.248		0.960

^a Silica-HPLC rel RT = retention time relative to 2378-TCDD (± 0.010). ^b GC packed column rel RT = retention time relative to ¹⁴C-2378-TCDD (± 0.008). ^c See text for recovery information. ^d Native 2378-TCDD elutes slightly later than ¹⁴C-2378-TCDD. ^e Related isomers typically reported as a total. ^f Fractions typically combined prior to GC-LRMS analysis.

TCDD isomers, we intentionally fortified a second portion of municipal sludge with each TCDD isomer at the levels shown in Table VI. Neither 1237- or 1238-TCDD was added due to their natural presence at 230 ppt (see Table V). Analysis of the fortified sample yielded the recovery data shown in Table VI. Regarding the 2378-TCDD data, the amount found was corrected for the recovery of the ¹⁴C-2378-TCDD and also for the 20 ppt natural 2378-TCDD previously observed in

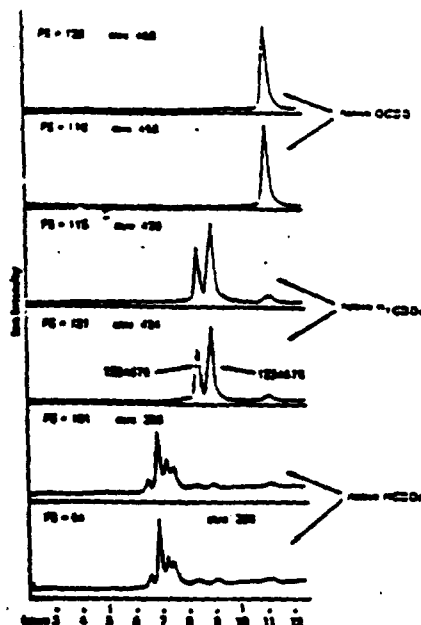


Figure 2. Higher chlorinated dioxin GC-LRMS mass chromatograms for electrostatic fly ash.

the sample. These data indicate that no other TCDD isomer interferes with the determination of 2378-TCDD when this analytical procedure is used. Recovery values given for all other TCDD isomers represent absolute observed values and were corrected for natural levels when necessary as listed in Table VI.

Typical temperature programmed GC-LRMS mass chromatograms for the determination of higher chlorinated dioxins appear in Figure 2. For the analysis of electrostatically precipitated fly ash the RP-HPLC HCDDs, H₇CDDs, and OCDD fractions were combined prior to GC-LRMS examination (see Figure 3c). As a means of overcoming problems associated with samples having relatively large amounts of native chlorinated dioxins compared to the 1-20 ng of fortified internal standards, a complete method validation study was conducted for HCDDs, H₇CDDs, and OCDD ranging from 50 ppt to 10 ppm ($\mu\text{g/g}$) and from 10 ppt to 5 ppb for 2378-TCDD. The control particulate sample used was a sandy loam soil, to which was added $\sim 150 \mu\text{L}$ of Mobile 1 synthetic engine lubricant per 20 g, as a means of increasing the total organics content to better simulate typical particulates. The following native CDD standards were used for sample fortification: 2378-TCDD, 123678-HCDD, 123679/123689-HCDD (Sil rel RT 1.039), 1234678-H₇CDD, and OCDD. The results of this

Table IV. Chlorinated Dioxins Observed in Environmental Particulate Samples

CDDs	reagent blank, ng	parts per billion				
		industrial dust	electrostatic fly ash	municipal sludge	European fly ash	NBS urban particulates
2378-TCDD + 4 isomers ^a	ND (0.08)	...	1.5 ^b	0.12 (0.12) ^c
other TCDDs (17 isomers)	ND (0.04)	0.16 (0.08)
HCDDs ^d (10 isomers)	ND (0.18)	ND (14)	14	2.1	350 ^d	2 (2)
1234679-H ₇ CDD ^e	ND (0.14)	200	11	14	470	16
1234678-H ₇ CDD ^e	ND (0.14)	220	17	15	870	18
OCDD ^e	ND (0.29)	4000	30	180	680	220

^a RP-HPLC RP-2378 fraction analyzed directly by GC-LRMS and not isomer specific as described in text. ^b Sample fully fractionated for isomer-specific results given in Table V. ^c Observed values without correction run as part of validation work reported in Table VII. ^d For "semi" isomer specific see Table VIII. ^e ¹⁴C-2378-TCDD recovery 78% and value listed has been corrected, see Table V for others, and ND = compound not detected at limit of detection in parentheses and no parentheses indicates detected signal $> 10\times$ limit of detection.

Table V. Isomer-Specific TCDD Analyses of Environmental Particulate Samples

TCDD isomer	reagent blank, pg	parts per trillion			
		industrial dust	electrostatic flyash	municipal sludge	European flyash
2378-TCDD ^a	ND (40)	1100	430 (110)	20 (2)	2200
1269-TCDD	ND (20)	ND (40)	190 (60)	ND (2)	1000 (140)
1469-TCDD	ND (20)	ND (50)	ND (50)	ND (2)	250 (140)
1267/1269-TCDD SU rel RT 1.623	ND (20)	ND (50)	190 (60)	ND (2)	300 (140)
1267/1269-TCDD SU rel RT 1.795	ND (20)	ND (50)	150 (80)	ND (2)	500 (140)
1268/1279-TCDD SU rel RT 1.233	ND (30) ^b	190 (90) ^c	1000 ^c
1269/1279-TCDD SU rel RT 1.291	ND (30)	ND (50)	310 (90)	3 (3) ^d	1300
1369/1478-TCDD SU rel RT 1.220
1369/1478-TCDD SU rel RT 1.340
1278-TCDD	ND (60)	ND (40)	ND (30)	ND (3)	3100
1236/1239-TCDD SU rel RT 1.356	ND (60)	ND (60)	250 (110)	ND (3)	1500
1236/1239-TCDD SU rel RT 1.350	ND (60)	ND (60)	150 (110)	ND (3)	800 (400)
1237/1238-TCDD SU rel RT 1.100	ND (60)	240 (50) ^e	720 ^e	220 ^e	8500 ^e
1237/1238-TCDD SU rel RT 1.123	ND (60)	ND (60) ^e	730 (110) ^e	ND (3) ^e	2000 ^e
1246/1249-TCDD SU rel RT 1.323	ND (60)	ND (60) ^e	730 (110) ^e	ND (3) ^e	1500
1246/1249-TCDD SU rel RT 1.411	ND (60)	ND (60) ^e	730 (110) ^e	ND (3) ^e	1500
1247/1248-TCDD SU rel RT 1.154	ND (60)	140 (50)	310 (70)	8 (2)	6900
1247/1248-TCDD SU rel RT 1.199	ND (60)	140 (50)	310 (70)	8 (2)	6900
1378-TCDD	ND (20)	560 (110)	1370 (150)	23 (5)	13200
1379-TCDD	ND (20)	1340	1160 (150)	13 (5)	7000
1368-TCDD	ND (20)	2780	1320 (150)	13 (5)	16200
1234-TCDD	ND (20)	180	370 (150)	ND (30)	2100
total TCDDs	ND	8340	7750	310	69500
¹⁴ C-2378-TCDD % recovery	83%	89%	84%	61%	56%

^a Corrected for ¹⁴C-2378-TCDD recovery and all other isomers are absolute observed. ^b = not recovered as described in text. ^c Observed but recovery questionable. ^d Detected on m/e 322 only. ^e Possible isomer interference as described in text.

Table VI. Isomer-Specific TCDD Analysis of Municipal Sludge after Fortification

TCDD isomer	concn in ppt		% recovery
	added	found	
2378-TCDD	143	140	98 ^a
1269-TCDD	150	108	72
1469-TCDD	166	122	73
1267/1269-TCDD SU rel RT 1.623	150	126	84
1267/1269-TCDD SU rel RT 1.795	171	145	85
1268/1279-TCDD SU rel RT 1.233	137 ^b	...
1268/1279-TCDD SU rel RT 1.291	140	89	49
1369/1478-TCDD SU rel RT 1.220	143
1369/1478-TCDD SU rel RT 1.340	151
1278-TCDD	160	104	65
1236/1239-TCDD SU rel RT 1.356	147	103	70
1236/1239-TCDD SU rel RT 1.350	146	80	55
1237/1238-TCDD SU rel RT 1.100	141	(180) ^c	...
1237/1238-TCDD SU rel RT 1.123	151	220 ^e	75
1246/1249-TCDD SU rel RT 1.323	151	220 ^e	75
1246/1249-TCDD SU rel RT 1.411	151	220 ^e	75
1247/1248-TCDD SU rel RT 1.154	131	203 ^e	69
1247/1248-TCDD SU rel RT 1.199	163	203 ^e	69
1378-TCDD	171	151	88
1379-TCDD	171	138	81
1368-TCDD	101	45	45
1234-TCDD	143	122	85

^a Corrected for recovery of ¹⁴C-2378-TCDD (72%) and native 2378-TCDD present given in Table V, all other isomers are absolute observed. ^b = not recovered as described in text. ^c Total not added. High native concentration given in Table V. ^d Absolute amount observed in this sample. ^e Total.

study appear in Table VII. These data indicate that the average recoveries of HCDDs, H₂CDDs, and OCDD over the described concentrations range are reasonably constant and are between 70 and 80%. Because typical particulate samples contain higher chlorinated CDDs within this range, recovery factors derived from the validation can be used. Since ¹⁴C-

labeled internal standards are added to all samples, whenever very low native concentrations are observed appropriate correction factors can be applied. Note that recovery values reported for TCDD have been corrected for the observed ¹⁴C-2378-TCDD internal standard recoveries after RP-HPLC fractionation.

Table VII. Chlorinated Dioxin Recovery and Precision Data for Fortified Sandy Loam Soil^a

sample no.	2378-TCDD ^b			HCDD			H.CDD			OCDD		
	added, ppt	found, ppt	%	added, ppt	found, ppt	%	added, ppt	found, ppt	%	added, ppt	found, ppt	%
1	10	13	130	50	30	60	50	46	92	200	160	80
2	20	23	140	100	72	72	100	73	73	400	320	80
3	20	21	105	100	87	87	100	85	85	400	260	65
4	50	49	98	250	160	64	250	170	68	1000	730	73
5	50	45	90	250	180	72	250	200	80	1000	820	82
6	50	51	102	250	170	68	250	200	80	1000	730	73
7	50	53	106	250	170	68	250	170	68	1000	720	72
8	50	50	100	250	190	76	250	210	84	1000	850	85
9	50	50	100	250	160	64	250	160	64	1000	700	70
10	50	47	94	250	180	72	250	180	72	1000	690	69
11	50	52	104	250	170	68	250	160	64	1000	690	69
12	100	97	97	500	410	82	500	430	86	2000	1900	95
13	100	109	109	500	440	88	500	460	92	2000	2060	103
14	5000	5350	107	1 x 10 ⁴	8.1 x 10 ³	81	5 x 10 ³	4.5 x 10 ³	90	10 x 10 ³	8.4 x 10 ³	84
15	5000	5400	108	1 x 10 ⁴	8.1 x 10 ³	81	5 x 10 ³	4.7 x 10 ³	94	10 x 10 ³	9.0 x 10 ³	90
\bar{x} all ^c			106			73			78			80
σ all ^c			13			10			11			11
\bar{x} prec ^d	50	49.6	99.2	250	173	69	250	181	72	1000	751	75
σ prec ^d		2.6	5.2		10.4	6.0		19.6	10.8		69.4	9.2

^a Data for all species obtained by GC-LRMS analysis of appropriate RP-HPLC fractions. 2378-TCDD values corrected for ¹⁴C-2378-TCDD internal standard recovery, other CDDs are absolute observed. ^b Corrected for ¹⁴C-2378-TCDD where average recovery was 89.8% for all samples. ^c \bar{x} all and σ all represent the mean and standard deviation of all samples. ^d \bar{x} prec and σ prec represent the mean and standard deviation of samples 4-11 to determine precision of the analysis.

Table VIII. "Semi" Isomer-Specific HCDD Analysis Data for European Flyash, Absolute Values Reported

HCDD isomer ^a	parts per billion	
	reagent blank	European Flyash
124679/124689-HCDD SU rel RT 0.958	ND (0.13) ^{b,c}	82 ^a
124679/124689-HCDD SU rel RT 0.972		
123468-HCDD	ND (0.13)	9 (9)
123678/123688-HCDD SU rel RT 0.970	ND (0.13) ^c	260 ^a
123678/123688-HCDD SU rel RT 1.039		
123469-HCDD		
123478-HCDD	ND (0.13) ^c	110 ^a
123678/123789-HCDD SU rel RT 0.974		
123678/123789-HCDD SU rel RT 1.060	ND (0.13) ^c	85 (9) ^a
123467-HCDD		

^a HCDD SU rel RT = retention time relative to 2378-TCDD by silica-HPLC (Table II). ^b ND (0.13) is not detected with limit of detection in ppb based on flyash sample size. ^c Total.

GC-LRMS analysis data for higher chlorinated CDDs appear in Tables IV and VIII. Table VIII illustrates a format for HCDD determination that is "semi"-isomer specific. In this case, the total RP-HCDDs fraction was analyzed directly by packed-column GC-LRMS. However, because GC rel RTs have been experimentally determined (see Table II) for all 10 individual HCDD isomers, we can separate the HCDDs observed into five distinct groups. Within each group only a limited number of isomers are possible. These analyses are accomplished by using isothermal column condition (-270 °C) so as to maximize the separation power of the column and to improve relative retention time measurements.

CONCLUSIONS

Although this paper demonstrates the applicability of a multiple-step procedure to isomer-specifically determine a variety of CDDs in environmental particulate samples, we have also applied the technique to many other matrices successfully. Simple modification of the preliminary matrix extraction has permitted the analysis of tissues, human milk, vegetable matter, chemical products, and wastes without sacrificing high sensitivity or isomer specificity. This procedure, utilizing packed-column GC-LRMS, has provided reliable results for several heavily contaminated matrices where the combination

of a less sophisticated cleanup followed by both packed and capillary column GC-HR MS has failed. Interested individuals may request a more thorough discussion of the method development experiments from the authors.

ACKNOWLEDGMENT

The authors express their gratitude to O. Hummer for graciously supplying the European fly ash sample and to R. Bumb, W. Crummett, and V. Stanger for their help in repairing this manuscript.

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RECEIVED for review January 23, 1980. Resubmitted May 14, 1980. Accepted July 31, 1980.

Secondary Ion Mass Spectra of Diquaternary Ammonium Salts

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Molecular dications emitted by momentum transfer processes are observed in secondary ion mass spectra (SIMS) of diquaternary ammonium salts. The relationship between molecular structure and the observation of dications is explored. Large intercharge separations, corresponding to lessened intramolecular coulombic repulsions, are observed to correlate with dication detection. Fragmentation with charge separation is facilitated by small intercharge distances and can preclude observation of the dication. Electron attachment to yield the monocation is an alternative to dication emission when the structure of the dication facilitates reduction. This occurs, for example, for the herbicide diquat (*N,N'*-ethylene-2,2'-bipyridyl dibromide) which is detected as its monocation. Complete spectra of diquaternaries can be taken with nanogram size samples.

Secondary ion mass spectrometry (SIMS) has recently been shown to be a sensitive method for the characterization of organic salts (1-6). Reported here is the observation of intact organic dications emitted from diquaternary ammonium salts upon sputtering. This constitutes the first observation of multiply charged organic molecular ions in SIMS. The result is of interest with regard to both analytical applications of SIMS and the fundamentals of ionization during sputtering. Specifically, some biologically important compounds, such as the herbicides paraquat and diquat and the curare alkaloids, have the diquaternary structure, so that SIMS may facilitate their characterization. In addition, studies on organic dications reflect the degree to which electron attachment occurs during sputtering. This process yields observable charged products for dications, but neutrals are sputtered when monocations are reduced during ion bombardment.

EXPERIMENTAL SECTION

All compounds were synthesized by using standard methods for the preparation of quaternary ammonium salts. The organic salts were burnished onto a 1 cm² roughened foil of either silver

or platinum prior to SIMS analysis using argon primary ions at 8 keV and 0.3-0.5 nA primary ion current. Beam diameter was approximately 1 mm and pressures in the ultra-high-vacuum chamber remained below 1×10^{-8} torr during the course of the experiments.

All spectra were taken with Ribet SIMS system using a quadrupole mass analyzer, Channeltron electron multiplier, and pulse-counting electronics.

Intercharge distances were measured by using Dreading model; charge localization on nitrogen was assumed and the maximum distance in the unstrained molecule is reported. Intercharge distances (*r*) were used to calculate coulombic repulsive energies (*T*) from $T \text{ (eV)} = 14.6/r \text{ (Å)}$.

RESULTS AND DISCUSSION

The SIMS spectrum of *N,N'*-bis(dimethyl)-4,4'-trimethylenedipiperidine diiodide (1) is shown in Figure 1. This spectrum provides both the molecular weight (inferred from the highest mass doubly charged ion, 268²⁺) and structural information on the compound. Emission of the doubly charged species is confirmed by the observation of the ¹³C isotope peak one-half mass unit above the dication peak (*m/z* 134.5 in Figure 2). Changing the counterion does not affect the SIMS spectrum; for example, the dibromide and diiodide of compound 1 gave identical SIMS spectra.

Analogous results were obtained for *N,N'*-bis(ethylmethyl)-4,4'-trimethylenedipiperidine diiodide (2) and for the aromatic compounds *N,N'*-bis(trimethyl)-4,4'-methylenedianiline diiodide (3) and *N,N'*-bis(dimethylethyl)-4,4'-methylenedianiline diiodide (4). The spectrum of compound 3 is shown in Figure 3; the dication, 284²⁺ at *m/z* 142 is of relatively low abundance, but its ¹³C isotope is well resolved in high-resolution scans.

A considerable number of diquaternary salts (5-19, Table I) did not exhibit observable dications. Compounds 18 and 19, while they did not yield molecular dications, did show the corresponding singly charged ions in their SIMS spectra. Compounds 5-17 may fail to exhibit dications because they fragment by a favorable charge separation route, $M^{2+} \rightarrow M_1^+ + M_2^+$. This is indicated by the absence of both singly and doubly charged molecular ions for these samples.

APPENDIX II

temperature of the water bath to 85 to 90°C. Concentrate the extract as in section 11.2.6 except use hexane to prewet the column. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of hexane.

11.2.8 Add a clean boiling chip to the concentrator tube and attach a two-ball micro-Snyder column. Prewet the column by adding about 1 mL of hexane to the top. Place the micro-K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5 to 10 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of the liquid reaches about 0.5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes. Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with 0.2 mL hexane. Proceed to section 11.3.2. If further processing is to be delayed, the extract should be quantitatively transferred to a Teflon sealed screw-cap vial and store refrigerated and protected from light.

11.2.9 Fill the sample bottle with water to the mark and measure the volume to the nearest 10 mL in a 1 L graduated cylinder.

11.3 Column Chromatograph

11.3.1 Column Preparation

11.3.1.1 Column 1: Place 1.0 g of silica gel into a 1 cm x 20 cm column and tap the column gently to settle the silica gel. Add 2 g sodium hydroxide-impregnated silica gel, 1 g silica gel, 4.0 g of sulfuric acid-impregnated silica gel, and 2 g silica gel. Tap column gently after each addition.

11.3.1.2 Column 2: Place 6.0 g of alumina into a 1 cm x 30 cm column and tap the column gently to settle the alumina. Add a 1-cm layer of purified sodium sulfate to the top of the alumina.

11.3.1.3 Add hexane to each column until the packing is free of channels and air bubbles. A small positive pressure (5 psi) of clean nitrogen can be used if needed.

11.3.2 Quantitatively transfer the hexane sample extract from the concentrator tube to the top of the silica gel in Column 1. Rinse the concentrator tube with two 0.5 mL portions of hexane; transfer rinses to Column 1.

- 11.3.3 With 90 mL of hexane, elute the extract from Column 1 directly into Column 2 containing alumina and sodium sulfate.
- 11.3.4 Add 20 mL of hexane to Column 2 and elute until the hexane level is just below the top of the sodium sulfate; discard the eluted hexane.
- 11.3.5 Add 20 mL of 20% methylene chloride/80% hexane (volume/volume) to Column 2 and collect the eluate.
- 11.3.6 Reduce the volume of the eluate with a gentle stream of filtered dry nitrogen. When the volume of the eluate is about 1 to 2 mL, transfer the eluate to the Carbowack column (Section 11.4.4). Rinse the eluate container with two 0.5 mL portions of hexane; transfer the rinses to the Carbowack column. CAUTION: Do not evaporate the sample extract to dryness. NOTE: The carbowack cleanup is not required for water samples unless needed to meet detection sensitivity criteria.

11.4 Carbowack Column Chromatography Procedure

- 11.4.1 Thoroughly mix 3.6 g of Carbowack C (or equivalent) with 16.4 g of Celite 345 (or equivalent) in a 40 mL vial and activate by heating in an oven at 130°C for 6 hours. Store in a desiccator. CAUTION: Check each new batch of mixed Carbowack/Celite to ensure TCDD recovery of >50%. Subject the low level concentration calibration solution to this procedure and measure the quantity of labeled and unlabeled 2,3,7,8-TCDD.
- 11.4.2 Insert a small plug of glass wool into a disposable pipet approximately 15 cm long by 7 mm O.D. Apply suction with a vacuum aspirator attached to the pointed end of the pipet, and add the Carbowack/Celite mixture until a 2 cm packing is obtained.
- 11.4.3 Pre-elute the column with:
 - 11.4.3.1 2 mL toluene
 - 11.4.3.2 1 mL of mixture of 75% (by volume) methylene chloride, 20% methanol and 5% benzene
 - 11.4.3.3 1 mL of 50% (by volume) cyclohexane and 50% methylene chloride
 - 11.4.3.4 2 mL of hexane
- 11.4.4 While the column is still wet with hexane add the sample extract from section 11.2.6. Elute the column with the following sequence of solvents and discard the eluates.

11.4.4.1 2 mL hexane

11.4.4.2 1 mL of 50% (by volume) cyclohexane and 50% methylene chloride

11.4.4.3 1 mL of 75% (by volume) methylene chloride, 20% methanol and 5% benzene

11.4.5 Elute with 2 mL of toluene and collect the eluate, which contains the TCDD. Transfer the rinses to a 1-mL amber vial with conical reservoir with further concentration as necessary. CAUTION: Do not evaporate the sample extract to dryness.

11.3.6 Store the sample extract in the dark at 4°C until just before GC/MS analysis.

11.5 GC/MS Analysis

11.5.1 Remove the sample extract or blank from storage and allow it to warm to ambient laboratory temperature. With a stream of dry, filtered nitrogen, reduce the extract/blank volume to near dryness. Immediately before GC/MS analysis, add 5 μ L of the 10 ng/ μ L recovery standard solution and adjust the extract or blank volume to 50 μ L with isooctane.

11.5.2 Inject a 2- μ L aliquot of the extract into the GC, operated under conditions previously used (Section 9) to produce acceptable results with the performance check solution.

11.5.3 Acquire mass spectral data for the following selected characteristic ions: m/z 259, 320, and 322 for unlabeled 2,3,7,8-TCDD; m/z 328 for $^{37}\text{Cl}_4$ -2,3,7,8-TCDD; and m/z 332 and 334 for $^{13}\text{C}_{12}$ -2,3,7,8-TCDD and $^{13}\text{C}_{12}$ -1,2,3,4-TCDD. Use the same data acquisition time and MS operating conditions previously used (Section 9.2.6) to determine response factors.

11.6 Identification Criteria. NOTE: Refer to Exhibit E, Section 7, for application of identification criteria.

11.6.1 Retention time (at maximum peak height) of the sample component must be within 3 seconds of the retention time of the $^{13}\text{C}_{12}$ -2,3,7,8-TCDD. Retention times are required for all chromatograms, but scan numbers are optional. These parameters should be printed next to the appropriate peak.

11.6.2 The integrated ion currents detected for m/z 259, 320, and 322 must maximize simultaneously. If there are peaks that will affect the maximization or quantitation of peaks of interest, attempts should be made to narrow the scan window to eliminate the interfering peaks. This should be reported on a separate chromatogram.

- 11.6.3 The integrated ion current for each analyte and surrogate compound ion (m/z 259, 320, 322 and 328) must be at least 2.5 times background noise and must not have saturated the detector; internal standard ions (m/z 332 and 334) must be at least 10 times background noise and must not have saturated the detector.
- 11.6.4 Abundance of integrated ion counts detected for m/z 320 must be $\geq 67\%$ and $\leq 90\%$ of integrated ion counts detected for m/z 322.
- 11.6.5 Abundance of integrated ion counts detected for m/z 332 must be $\geq 67\%$ and $\leq 90\%$ of integrated ion counts detected for m/z 334.
- 11.6.6 The recovery of the internal standard $^{13}\text{C}_{12}$ -2,3,7,8-TCDD should be within a 40 percent to 120 percent recovery window. This is an advisory limit only, an action window may be set when sufficient data is available.

12. CALCULATIONS

12.1 Concentration

- 12.1.1 Calculate the concentration of 2,3,7,8-TCDD using the formula:

$$C_x = \frac{A_x \cdot Q_{is}}{A_{is} \cdot RPF_n \cdot W}$$

where C_x = 2,3,7,8-TCDD concentration in ug/kg or ug/L

A_x = the sum of integrated ion abundance detected for m/z 320 and 322

A_{is} = the sum of integrated ion abundances detected for m/z 332 and 334 (characteristic ions of $^{13}\text{C}_{12}$ -2,3,7,8-TCDD, the internal standard)

Q_{is} = quantity (in ng) of $^{13}\text{C}_{12}$ -2,3,7,8-TCDD added to the sample before extraction

RPF_n = calculated mean response factor for unlabeled 2,3,7,8-TCDD relative to $^{13}\text{C}_{12}$ -2,3,7,8-TCDD

W = weight (in g) of wet soil or sediment sample or volume of water extracted (in mL).

12.1.2 If the calculated concentration of unlabeled 2,3,7,8-TCDD exceeds 100 ug/kg for soil/sediment or 1 ug/L for water, which is the maximum concentration of the concentration calibration solutions, the linear range may have been exceeded, and a smaller aliquot of that sample must be analyzed. Accurately weigh to three significant figures a 1-g aliquot of the wet soil/sediment or measure a 100 mL aliquot of water. Add the 1.5 mL acetone dilution of 100 uL of the sample fortification solution (Section 7.8), just as for the larger sample aliquot. Extract and analyze.

12.1.3 Calculate the concentration of the internal standard $^{13}\text{C}_{12}$ -2,3,7,8-TCDD using the formula:

$$C_{is} = \frac{A_{is} \cdot Q_{rs}}{A_{rs} \cdot RF_1 \cdot W}$$

where

C_{is} = concentration of $^{13}\text{C}_{12}$ -2,3,7,8-TCDD in ug/kg or ug/L

A_{is} = sum of integrated ion abundances for m/z 332 and 334 for $^{13}\text{C}_{12}$ -2,3,7,8-TCDD

A_{rs} = sum of integrated ion abundances for m/z 332 and 334 for $^{13}\text{C}_{12}$ -1,2,3,4-TCDD

Q_{rs} = quantity (in ug) of $^{13}\text{C}_{12}$ -1,2,3,4-TCDD added to the sample before injection

RF_1 = calculated mean response factor for $^{13}\text{C}_{12}$ -1,2,3,4-TCDD

W = weight (in g) of wet soil or sediment sample or volume of water extracted (in mL).

12.2 Estimated Maximum Possible Concentration — For samples in which no unlabeled 2,3,7,8-TCDD was detected, calculate the estimated maximum possible concentration, which is the concentration required to produce a signal with peak height of 2.5 times the background signal level. The background level is determined by measuring the range of the noise (minimum to maximum) for either m/z 320 or 322 in the appropriate region of the SICP (as defined in section 1.3.11), multiplying that noise height by 2.5, and relating the product height to an estimated concentration that would produce that product height.

Use the formula:

$$MPC = \frac{2.5 \cdot A_x \cdot Q_{1s}}{A_{1s} \cdot RF_n \cdot W}$$

where MPC = estimated maximum possible concentration of unlabeled 2,3,7,8-TCDD required to produce A_x in ug/kg or ug/L

A_x = peak height for either m/z 320 or 322 within + 5 scans of the internal standard peak used to measure A_{1s}

A_{1s} = peak height of the appropriate ion characteristic of the internal standard, m/z 332 when m/z 320 is used to determine A_x , and m/z 334 when m/z 322 is used to determine A_x

Q_{1s} , RF and W retain the definitions previously stated in Section 12.1.1

12.4 The relative percent difference (RPD) is calculated as follows: (See Section 5.1.1, Exhibit E.)

$$RPD = \frac{S_1 - S_2}{\text{Mean Concentration}} \times 100 = \frac{|S_1 - S_2|}{\frac{S_1 + S_2}{2}} \times 100$$

S_1 and S_2 represent sample and duplicate sample results.

12.6 Percent Recovery of 2,3,7,8-TCDD in spiked field blanks =

$$\frac{\text{concentration found}}{\text{concentration added}} \times 100$$

12.7 Percent Recovery of internal standard, $^{13}C_{12}$ -2,3,7,8-TCDD =

$$\frac{\text{concentration found}}{\text{concentration added}} \times 100$$

$$12.8 \text{ Standard deviation} = S = \sqrt{\frac{\sum_{i=1}^N (X_i - \bar{X})^2}{N - 1}}$$

12.9 Percent relative standard deviation =

$$\frac{\text{Standard Deviation}}{\text{Mean}} \times 100 = \frac{S}{\bar{X}} \times 100$$

APPENDIX III

- 1.7.1.2 Immediately after weighing the sample for extraction, weigh 5-10 g of the sediment into a tared crucible. Determine the percent moisture by drying overnight at 105°C. Allow to cool in a desiccator before weighing. Concentrations of individual analytes will be reported relative to the dry weight of sediment.

$$\frac{\text{lb of sample} - \text{gm of dry sample}}{\text{gm of sample}} \times 100 = \text{moisture}$$

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APPENDIX IV

Tetra-Octa CDD/CDF Scan Quantitation Protocol and Analytical Standards

- Minimal Requirements for Bidders

Analytical Standards

- 2378 TCDD, $^{13}\text{C}_{12}$, $^{37}\text{Cl}_4$
- 2378 TCDF
- Mixture of TCDD isomers to verify column resolution *
- OCDD, $^{13}\text{C}_{12}$ -OCDD
- Mix of Penta CDD/CDF, Hexa CDD/CDF, Hepta CDD/CDF to establish RT windows for spiking. *Continuing calibrations must be within RT windows established.*

Quantitation

Quantitate TCDD, TCDF, Penta CDD, Penta CDF, Hexa CDD, Hexa CDF
against $^{13}\text{C}_{12}$ -2378-TCDD

(Quantitate TCDF, Penta CDF, and Hexa CDF against $^{13}\text{C}_{12}$ -TCDF, ~~if available~~)

Quantitate Hepta CDD, Hepta CDF, OCDD, OCDF against $^{13}\text{C}_{12}$ -OCDD

Qualify data as "estimated" concentrations with tentative identifications unless you have access to pure isomer standards (i.e., all 38 TCDF isomers, etc.)

WA-56K357
* Column resolution should meet Dioxin IFB ~~WA84-A002~~ criteria i.e. 25% valley or lower between 2,3,7,8-TCDD and it's nearest neighbor in SIC display (Appendix VII).

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APPENDIX V

DELIVERABLES REQUIRED FOR GC/MS DIOXIN/FURAN ANALYSIS

A. SAMPLE PREPARATION AND METHOD DOCUMENTATION

- (1) "Cookbook" style step-by-step method including instrument/conditions, type and source of reagents.
- (2) Analyst bench records describing dilutions, weighings and any unusual occurrences during prep, extraction or clean up.
- (3) Calculations and method used in determination of percent lipids and percent solids (where applicable).

B. DIOXIN/FURAN QUANTITATION AND IDENTIFICATION DOCUMENTATION

- (1) Detailed explanation of the quantitation and identification procedure used for all isomer classes and specific isomers.
- (2) List of criteria for positive identification of 2,3,7,8-TCDD and 2,3,7,8-TCDF.
- (3) Example calculations of response ratios, sample results and detection limits.
- (4) Simultaneous display/offset SICs and peak areas of native, $^{13}\text{C}_{12}$ - and $^{37}\text{Cl}_4$ -2,3,7,8-TCDD in all samples and QC, including blanks.
- (5) Simultaneous display/offset SICs and peak areas of ions monitored for each PCDD/PCDF class.
- (7) List of exact ion masses for each isomer/class, current and historical response factors and retention times for positive ID.
- (8) Simultaneous display/offset SICs to check for polychlorinated diphenylethers which may co-elute with the furans.
- (9) Simultaneous display/offset SICs of M/Z 257, 259 in samples with positive 2, 3, 7, 8-TCDD content.
- (10) Simultaneous display/offset SICs and peak areas of ions monitored, for all standards used, for each PCDD/PCDF class. Include a listing of response ratios, ion ratios and amount of each standard used.

(11) Chronological List (date/time) of all standards, native spikes, method blanks, duplicates, samples, reanalyses etc.

(12) Completed copy (including sample condition) of SAS packing List.

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APPENDIX VI

CASE 1

PCDD/PCDF Concentration (PPT) as Dry Weight

ISOMER OR NOMOLOG	DATE:	ALIQOT WT. (g)	DATE:	ALIQOT WT. (g)	PRECISION AS RPD	PRECISION LIMITS	COMMENTS
	Samp. #		Samp. #				
2,3,7,8-TCDF							
3/CI-2,3,7,8-TCDF							
% Recovery							
ng 3/CI-2,3,7,8-TCDF							
Added							
Total TCDFs							
Total Penta CDFs							
Total Hexa CDFs							
Total Hepta CDFs							
OCDF							

2,3,7,8-TCDD							
3/CI-2,3,7,8-TCDD							
% Recovery							
ng 3/CI-2,3,7,8-TCDD							
Added							
Total Tetra CDDs							
Total Penta CDDs							
124679 & 124689							
H ₆ CDD							
123679 & 123689							
H ₆ CDD							
123469 H ₆ CDD							
123478 H ₆ CDD							
123678 H ₆ CDD							
123467 & 123709							
H ₆ CDD							
Total H ₆ CDDs							
3/CI-123478 H ₇ CDD							
% Recovery							
ng 3/CI-1232478							
H ₇ CDD Added							
1234679 H ₇ CDD							
1234678 H ₇ CDD							
TOTAL H ₇ CDD							
OCDD							
3/CI-OCDD % Recovery							
ng 3/CI-OCDD Added							

APPENDIX VII

DS-66 CROSS SCAN REPORT, RUN: GCHXC0001

• TIC

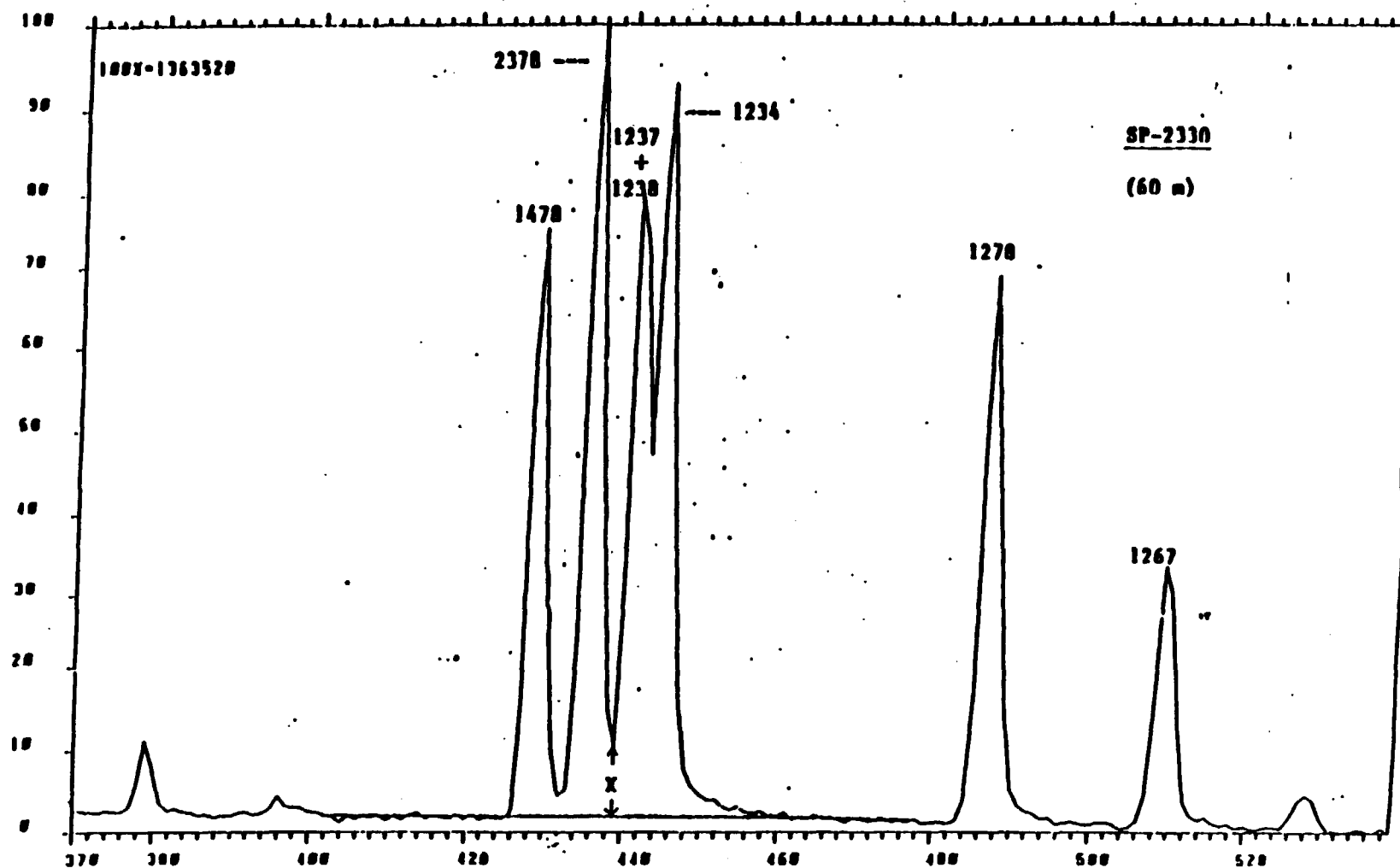


Figure 2. Selected ion current profile for m/z 320 and 322 produced by MS analysis of performance check solution using a 60-m SP-2330 fused silica capillary column and conditions listed in Table I.

DS-55 CROSS SCAN REPORT, RUN: SIL20002

• TIC

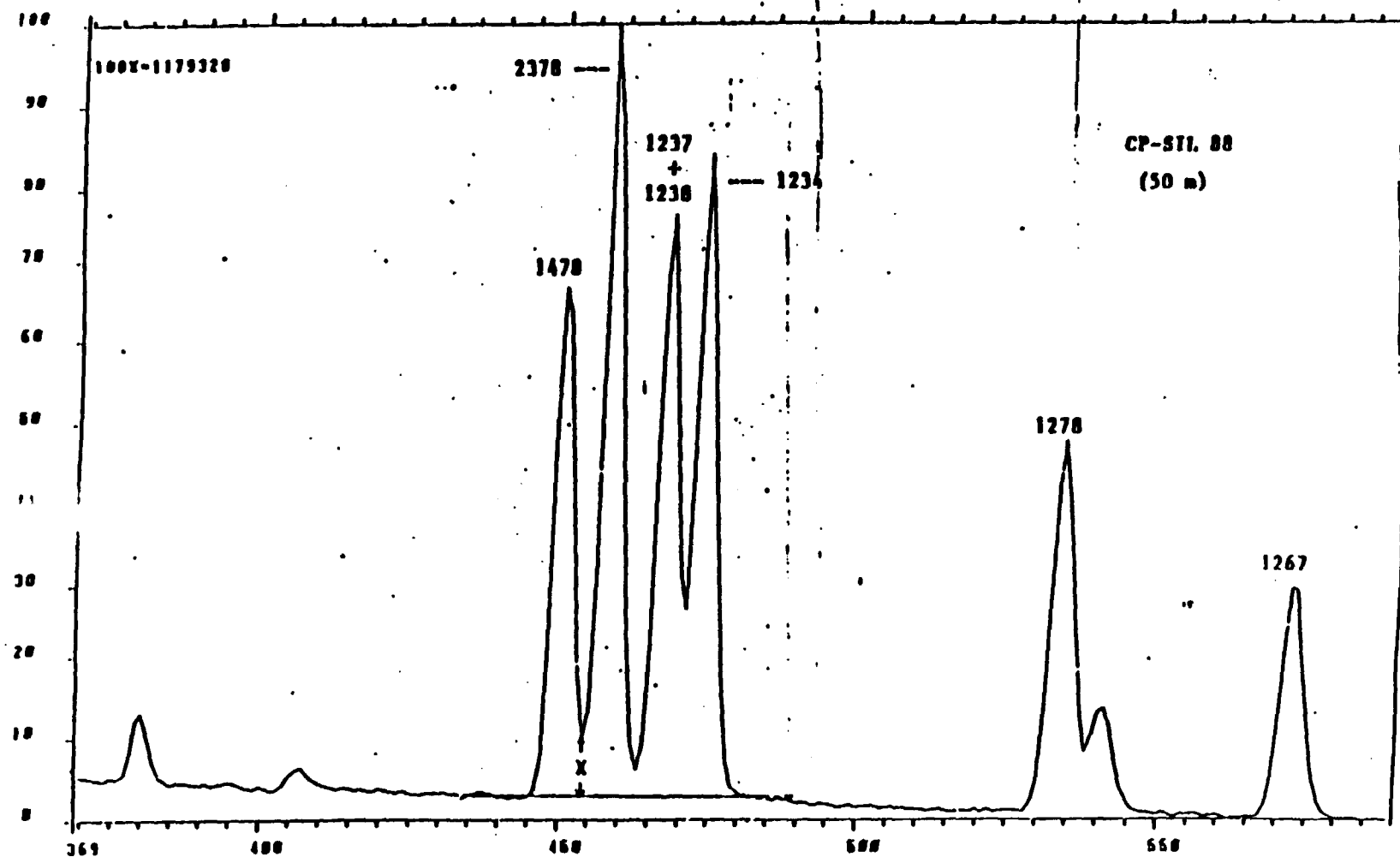


Figure 3. Selected ion current profile for m/z 320 and 322 produced by MS analysis of performance check solution using a 50-m CP-SIL 88 fused silica capillary column and conditions listed in Table 1.

U.S. Environmental Protection Agency
CLP Sample Management Office
P. O. Box 818, Alexandria, Virginia 22313
PHONE: (703)/557-2490 or FTS/557-2490

SAS Number

SPECIAL ANALYTICAL SERVICES
Client Request

☒ Regional Transmittal ☐ Telephone Request

A. EPA Region/Client: EPA Region V WW Engineering & Science
B. RSCC Representative: Jan Pels
C. Telephone Number: 312/ 353-2720
D. Date of Request: _____
E. Site Name: Skinner Landfill - West Chester, Ohio

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. General description of analytical service requested: Analysis of high hazard waste samples for Ultimate Analysis. This includes carbon, hydrogen, sulfur, nitrogen, ash, and oxygen by ASTM methods.

2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium, or high concentration):

58 High hazard waste samples.

Includes duplicates and blanks.

3. Purpose of analysis (specify whether Superfund (Remedial or Enforcement), RCRA, NPDES, etc.):

Superfund - Remedial Action

4. Estimated date(s) of collection: _____
5. Estimated date(s) and method of shipment: Daily by overnight carrier.
6. Number of days analysis and data required after laboratory receipt of samples:
Laboratory should report results within 30 days after receipt of samples.
7. Analytical protocol required (attach copy if other than a protocol currently used in this program):
Ultimate Analysis by ASTM D3176. This includes carbon and hydrogen by ASTM D317
nitrogen by ASTM D3179, sulfur by ASTM D3177, ash by ASTM D3174, and oxygen by
difference (ASTM D3176, Section 6.5). (see attached)

8. Special technical instruction (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.): _____
Samples may be toxic/flammable.
Analysis must be performed in conjunction with the Proximate Analysis SAS for this project

9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.). If not completed, format of results will be left to program discretion.
Supply copies of all raw data, bench sheets, sample calibration, and QA/QC for
each procedure. All records must be legible and sufficient to recalculate sample
values.
10. Other (use additional sheets or attach supplementary information, as needed):

11. Name of sampling/shipping contact: Bob Phillips
Phone: 616/ 942-9600

I. DATA REQUIREMENTS

<u>Parameter:</u>	<u>Detection Limit</u>	<u>Precision Desired</u> (<u>±% or Conc.</u>)
<u>Sulfur</u>	<u>less than 1%</u>	<u>+ 20%</u>
<u>Carbon/Hydrogen</u>	<u>less than 1%</u>	<u>+ 20%</u>
<u>Nitrogen</u>	<u>less than 1%</u>	<u>+ 20%</u>
<u>Ash</u>	<u>less than 1%</u>	<u>+ 20%</u>
<u>Oxygen</u>	<u>less than 1</u>	<u>by difference NA</u>
<u> </u>	<u> </u>	<u> </u>

II. QC REQUIREMENTS

<u>Audits Required</u>	<u>Frequency of Audits</u>	<u>Limits* (% or Conc.)</u>
<u>Blanks</u>	<u>1 per 10 samples</u>	<u>less than 1%</u>
<u>Duplicates</u>	<u>1 per 10 samples</u>	<u>+ 20%</u>
<u>NBS Standard</u>	<u>1 per 10 samples</u>	<u>+ 20% of true value</u>
<u>Reference Manual</u>	<u> </u>	<u> </u>
<u> </u>	<u> </u>	<u> </u>
<u> </u>	<u> </u>	<u> </u>
<u> </u>	<u> </u>	<u> </u>

III. ACTION REQUIRED IF LIMITS ARE EXCEEDED:

Rerun sample if blanks or duplicates exceed QC limits. Rerun entire set if
reference material exceeds QA/QC limits.

Contact: Jan Pels 312/ 353-2720 or Chuck Elly 312/ 353-9087

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for special analytical services. Should you have any questions or need any assistance, please call the Sample Management Office.



Designation: D 3176 - 84

Standard Method for Ultimate Analysis of Coal and Coke¹

This standard is issued under the fixed designation D 3176; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This method covers the term ultimate analysis as it is applied to the analysis of coal and coke. The information derived is intended for the general utilization by applicable industries, to provide the basis for evaluation, beneficiation, or for other purposes.

1.2 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of whoever uses this standard to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 ASTM Standards:

- D 346 Method of Collection and Preparation of Coke Samples for Laboratory Analysis²
- D 2013 Method of Preparing Coal Samples for Analysis²
- D 2234 Methods for Collection of a Gross Sample of Coal²
- D 2361 Test Method for Chlorine in Coal²
- D 2795 Test Methods for Analysis of Coal and Coke Ash²
- D 3172 Method for Proximate Analysis of Coal and Coke²
- D 3173 Test Method for Moisture in the Analysis Sample of Coal and Coke²
- D 3174 Test Method for Ash in the Analysis Sample of Coal and Coke from Coal²
- D 3177 Test Methods for Total Sulfur in the Analysis Sample of Coal and Coke²
- D 3178 Test Methods for Carbon and Hydrogen in the Analysis Sample of Coal and Coke²
- D 3179 Test Methods for Nitrogen in the Analysis Sample of Coal and Coke²
- D 4239 Test Method for Sulfur in the Analysis Sample of Coal and Coke using High Temperature Tube Furnace Combustion Methods²

3. Significance and Use

3.1 Summarizing the ash content and the content of the organic constituents in a specific format under the heading, *Ultimate Analysis*, provides a convenient and uniform system for comparing coals or cokes. This tabulation used with that of *Proximate Analysis* (Methods D 3172) permits cursory valuation of coals for use as fuel or in other

carbonaceous processes and of cokes for metallurgical purpose.

4. Definition

4.1 *ultimate analysis*—in the case of coal and coke, the determination of carbon and hydrogen in the material, as found in the gaseous products of its complete combustion, the determination of sulfur, nitrogen, and ash in the material as a whole, and the calculation of oxygen by difference.

NOTE 1—The determination of phosphorus or chlorine is not by definition a part of the ultimate analysis of coal or coke. See Test Method D 2361 for the determination of chlorine and Test Methods D 2795 for the determination of phosphorus.

NOTE 2—Moisture is not by definition a part of the ultimate analysis of coal or coke but must be determined in order that analytical data may be converted to bases other than that of the analysis sample.

NOTE 3—Inasmuch as some coals contain mineral carbonates, and practically all contain clay or shale containing combined water, a part of the carbon, hydrogen, and oxygen found in the products of combustion may arise from these mineral components.

5. General Requirements

5.1 Coal sample collection shall be in accordance with Methods D 2234, and sample preparation shall be in accordance with Method D 2013. Coke sampling and preparation shall be in accordance with Method D 346.

6. Specific Requirements

6.1 *Carbon and Hydrogen*—The carbon and hydrogen determination shall be made in accord with Test Method D 3178.

6.2 *Sulfur*—The sulfur determination shall be made in accordance with Test Method D 3177 or ~~3178~~.

6.3 *Nitrogen*—The nitrogen determination shall be made in accordance with Test Method D 3179.

6.4 *Ash*—The ash determination shall be made in accordance with Test Method D 3174.

6.5 *Oxygen*—There being no satisfactory direct ASTM method of determining oxygen, it shall be calculated by subtracting from 100 the sum of the other components of the ultimate analysis. The result so obtained is affected by errors incurred in the other determinations of the ultimate analysis and also by the changes in weight of the ash-forming constituents on ignition. By definition, oxygen calculated as a weight percentage of the analysis sample according to this procedure does not include oxygen in the mineral matter or in the ash, but does include oxygen in the free water (moisture) associated with the analysis sample. See Section 7 of this method for calculating and reporting results on other bases.

¹ This method is under the jurisdiction of ASTM Committee D-5 on Coal and Coke and is the direct responsibility of Subcommittee D05.21 on Methods of Analysis.

Current edition approved March 30, 1984. Published May 1984. Originally published as D 3176-74. Last previous edition D 3176-74 (1979).

² Annual Book of ASTM Standards, Vol 05.05.

TABLE 1 Procedures for Converting As-Determined Values to Other Bases

Reporting Basis Parameter ^a	As-Determined ^a	Dry	As-Received ^{c,d}	
			H_{ar} and Ox_{ar} include H and Ox in Moisture (M_{ar})	H_{ar} and Ox_{ar} do not include H and Ox as M_{ar}
Ash	No corrections (See standard method)	$P_d = P_{ad} \times \left(\frac{100}{100 - M_{ad}} \right)$	$P_{ar} = P_{ad} \times \left(\frac{100 - M_{ar}}{100 - M_{ad}} \right)$	same as column at left
Carbon	No corrections (See standard method)	$H_d = (H_{ad} - 0.1119M_{ad}) \times \left(\frac{100}{100 - M_{ad}} \right)$	$H_{ar} = \left[(H_{ad} - 0.1119M_{ad}) \times \left(\frac{100 - M_{ar}}{100 - M_{ad}} \right) + 0.1119M_{ar} \right]$	$H_{ar} = (H_{ad} - 0.1119M_{ad}) \times \left(\frac{100 - M_{ar}}{100 - M_{ad}} \right)$
Carbon (P)				
Sulfur				
Hydrogen (H)	No corrections (See standard method)	$H_d = (H_{ad} - 0.1119M_{ad}) \times \left(\frac{100}{100 - M_{ad}} \right)$	$H_{ar} = \left[(H_{ad} - 0.1119M_{ad}) \times \left(\frac{100 - M_{ar}}{100 - M_{ad}} \right) + 0.1119M_{ar} \right]$	$H_{ar} = (H_{ad} - 0.1119M_{ad}) \times \left(\frac{100 - M_{ar}}{100 - M_{ad}} \right)$
Oxygen (Ox)	$Ox_{ad} = 100 - A_{ad} - C_{ad} - H_{ad} - N_{ad} - S_{ad}$	$Ox_d = (Ox_{ad} - 0.8881M_{ad}) \times \left(\frac{100}{100 - M_{ad}} \right)$ or $Ox_d = 100 - A_d - C_d - H_d - N_d - S_d$	$Ox_{ar} = \left[(Ox_{ad} - 0.8881M_{ad}) \times \left(\frac{100 - M_{ar}}{100 - M_{ad}} \right) + 0.8881M_{ar} \right]$	$Ox_{ar} = (Ox_{ad} - 0.8881M_{ad}) \times \left(\frac{100 - M_{ar}}{100 - M_{ad}} \right)$

^a All parameters expressed on a weight percent basis.

^b Hydrogen and oxygen reported on as-determined basis include hydrogen and oxygen in free moisture associated with analysis sample.

^c Alternative procedures are shown, differing on the basis of whether hydrogen and oxygen in the moisture are included or are not included in the report values. A footnote or other means should be employed to indicate the basis used.

^d To convert results to a moisture-containing basis other than as-received, as for example equilibrium capacity moisture, substitute the appropriate moisture value for M_{ar} in the equations.

6.6 Moisture—The moisture determination shall be made in accordance with Test Method D 3173.

7. Calculating and Reporting Results

7.1 The results of an ultimate analysis may be reported on any of a number of bases, differing from each other in the manner by which moisture is treated.

7.2 To avoid ambiguity and to provide a means for conversion of data to bases other than the reported basis, it is essential that except for data reported on a dry basis, an appropriate moisture content be given in the data report.

7.3 It is recommended that for data reported on the as-received basis (or any other moist basis) a footnote or some other means be employed in the report to indicate whether the hydrogen and oxygen values reported do include or do not include the hydrogen and oxygen in the free water (moisture) associated with the sample.

7.4 Procedures for converting ultimate analysis sample data to other bases are presented in Table 1.

7.4.1 Symbols used in Table 1 are:

M = moisture, weight %,

P = a symbol used interchangeably in the table to refer to ash, or carbon, or nitrogen, or sulfur, weight %,

H = hydrogen, weight %, and

Ox = oxygen, weight %.

7.4.2 Subscripts used in Table 1 are:

ad = as-determined from analysis sample,

ar = as received or any other moisture-containing basis (that is, equilibrium capacity moisture basis, as-shipped moisture basis, bed moisture basis) if the appropriate moisture value is substituted for M_{ar} in the formulae, and

d = dry basis.

7.4.3 Hydrogen and oxygen on the as-determined basis include hydrogen and oxygen in free water (moisture) associated with the analysis sample. However, hydrogen and oxygen values reported on other moisture-containing bases may be reported either as containing or as not containing the hydrogen and oxygen in water (moisture) reported on that basis. Alternative conversion procedures are shown in Table 1.

7.5 An example of ultimate analysis data tabulated for a hypothetical coal on various bases is given in Table 2.

8. Reproducibility of Results

8.1 The permissible differences between two or more determinations shall not exceed the values given in Table 3

TABLE 2 Ultimate Analysis Data

Test Parameter	As-Determined		As-Received Basis	
	Hydrogen and oxygen include H and O ₂ in sample moisture (M_{ad})	Dry Basis	Hydrogen and oxygen include H and O ₂ in sample moisture (M_{ar})	Hydrogen and oxygen do not include H and O ₂ in sample moisture (M_{gr})
Carbon, weight %	60.06	66.02	46.86	46.86
Hydrogen, weight %	5.44	4.87	6.70	3.46
Nitrogen, weight %	0.88	0.97	0.69	0.69
Sulfur, weight %	0.73	0.80	0.57	0.57
Ash, weight %	7.86	8.64	6.13	6.13
Oxygen, weight % (by difference)	25.01	18.70	39.05	13.27
Total %	100.00	100.00	100.00	70.98
Total moisture, weight % (as-received)	(29.02)	29.02
Moisture weight % (samples as-determined)	9.00	Total % 100.00

(Air-Dry Loss in accordance with Method D 2013 = 22.00 %)

TABLE 3 Precision

	Permissible Differences, %	
	Same Laboratory	Different Laboratory
Sulfur:		
Coal, under 2 %	0.05	0.10
Coal, over 2 %	0.10	0.20
Coke	0.03	0.05
Carbon	0.3	...
Hydrogen	0.07	...
Nitrogen	0.05	...
Ash:		
No carbonates present	0.2	0.3
Carbonates present	0.3	0.5
Coals with more than 12 % ash, containing carbonates and pyrites	0.5	1.0

The American Society for Testing and Materials takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, 1916 Race St., Philadelphia, PA 19103.



Standard Test Methods for Total Sulfur in the Analysis Sample of Coal and Coke¹

This standard is issued under the fixed designation D 3177; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 These test methods cover two alternative procedures for the determination of total sulfur in samples of coal and coke. Sulfur is included in the ultimate analysis of coal and coke.

1.2 The procedures appear in the following order:

Method A—Eschka Method
Method B—Bomb Washing Method

Sections
6 to 9
10 to 11

1.3 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of whoever uses this standard to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Specific precautionary statements are given in Sections 11.1.1 to 11.1.1.7.

2. Referenced Documents

2.1 ASTM Standards:

- D 346 Method of Collection and Preparation of Coke Samples for Laboratory Analysis²
- D 1193 Specification for Reagent Water³
- D 2013 Method of Preparing Coal Samples for Analysis²
- D 2015 Test Method for Gross Calorific Value of Coal and Coke Fuel by the Adiabatic Bomb Calorimeter²
- D 3173 Test Method for Moisture in the Analysis Sample of Coal and Coke²
- D 3176 Method for Ultimate Analysis of Coal and Coke²
- D 3180 Method for Calculating Coal and Coke Analyses from As-Determined to Different Bases²
- D 3286 Test Method for Gross Calorific Value of Coal and Coke by the Isoperibol Bomb Calorimeter²
- E 144 Recommended Practice for Safe Use of Oxygen Combustion Bombs⁴

3. Summary of Methods

3.1 *Eschka Method*—A weighed sample and Eschka mixture are intimately mixed and ignited together. The sulfur is dissolved in hot water and then precipitated from the resulting solution as barium sulfate (BaSO_4). The precipitate is filtered, ashed, and weighed.

3.2 *Bomb Washing Method*—Sulfur is precipitated as BaSO_4 from oxygen-bomb calorimeter washings, and the precipitate is filtered, ashed, and weighed.

4. Significance and Use

4.1 Determination of sulfur is, by definition, part of the ultimate analysis of coal.

4.2 Sulfur analysis results obtained by these methods are used to serve a number of interests: evaluation of coal preparation, evaluation of potential sulfur emissions from coal combustion or conversion processes, evaluation of the coal quality in relation to contract specification, and other purposes of commercial or scientific interest.

5. Sample

5.1 The sample shall be the material pulverized to pass No. 60 (250- μm) sieve. Weigh and record the percent passing through the sieve.

5.2 A separate portion of the analysis sample should be analyzed for moisture content in accordance with Test Method D 3173, so that calculation to other than the as-determined basis can be made.

5.3 Procedures for converting as-determined sulfur values obtained from the analysis sample to other bases are described in Method D 3176 and Method D 3180.

5.4 Standard Reference Material (SRM), such as SRM Nos. 2862 through 2685—Sulfur in Coal⁵ which consist of four different coals that have been individually crushed and ground to pass a 60-mesh sieve, and bottled in 50-g units, or other commercially available reference material coals with a certified sulfur content of $\pm 0.0\text{xx}$ precision can be used. Sulfur values obtained by analyzing these coals, using any of the methods described in this test method, may be used for checking the accuracy of analytical results.

ALTERNATIVE PROCEDURES

METHOD A—ESCHKA METHOD

6. Apparatus

6.1 *Gas (Note 1) or Electric Muffle Furnace, or Burners*, for igniting the sample with the Eschka mixture and for igniting the barium sulfate (BaSO_4).

NOTE 1—Gas may contain sulfur compounds.

6.2 *Crucibles or Capsules*—Porcelain capsules, $\frac{7}{8}$ in. (22 mm) in depth and $1\frac{3}{4}$ in. (44 mm) in diameter, or porcelain crucibles of 30-mL capacity, high or low form, or platinum crucibles of similar size shall be used for igniting the sample

¹ These test methods are under the jurisdiction of ASTM Committee D-5 on Coal and Coke and are the direct responsibility of Subcommittee D05.21 on Methods of Analysis.

Current edition approved Jan. 27, 1984. Published March 1984. Originally published as D 3177 - 73. Last previous edition D 3177 - 82.

² Annual Book of ASTM Standards, Vol 05.05.

³ Annual Book of ASTM Standards, Vol 11.01.

⁴ Annual Book of ASTM Standards, Vol 14.02.

⁵ Available from the Office of Standard Reference Materials, Room B314 Chemistry Bldg., National Bureau of Standards, Washington, DC 20234.

with the Eschka mixture. Porcelain, platinum, alundum, or silica crucibles of 10 to 15-mL capacity, shall be used for igniting the BaSO_4 .

7. Reagents

7.1 Purity of Reagents—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Available Reagents of the American Chemical Society, where such specifications are available.⁶ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 Purity of Water—Unless otherwise indicated, references to water shall be understood to mean reagent water, Type IV, conforming to Specification D 1193.

7.3 Barium Chloride Solution (100 g/L)—Dissolve 100 g of barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) and dilute to 1 L with water.

7.4 Eschka Mixture—Thoroughly mix 2 parts by weight of light calcined magnesium oxide (MgO) with 1 part of anhydrous sodium carbonate (Na_2CO_3). Both materials should be as free as possible from sulfur. Eschka mixture is also available commercially.

7.5 Hydrochloric Acid (1+1)—Mix equal volumes of concentrated hydrochloric acid (HCl , sp gr 1.19) and water.

7.6 Hydrochloric Acid (1+9)—Mix 1 volume of concentrated hydrochloric acid (HCl , sp gr 1.19) with 9 volumes of water.

7.7 Methyl Orange Indicator Solution (0.2 g/L)—Dissolve 0.02 g of methyl orange in 100 mL of hot water and filter.

7.8 Sodium Carbonate, Saturated Solution—Dissolve approximately 60 g of crystallized sodium carbonate ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$) or 22 g of anhydrous sodium carbonate (Na_2CO_3) in 100 mL of water, using a sufficient excess of Na_2CO_3 to ensure a saturated solution.

7.9 Sodium Hydroxide Solution (100 g/L)—Dissolve 100 g of sodium hydroxide (NaOH) in 1 L of water. This solution may be used in place of the Na_2CO_3 solution.

8. Procedure

8.1 Preparation of Sample and Mixture—Thoroughly mix on glazed paper approximately 1 g of the sample, weighed to nearest 0.1 mg and 3 g of Eschka mixture. The amount of sample to be taken will depend on the amount of BaCl_2 solution required in accordance with 8.3. Transfer to a porcelain capsule, or porcelain crucible, or a platinum crucible and cover with about 1 g of Eschka mixture.

8.2 Ignition—Heat the crucible over an alcohol, gasoline, or gas flame as described in 8.2.1, or in a gas or electrically heated muffle as described in 8.2.2 for coal and in 8.2.3 for coke. The use of artificial gas for heating the sample and the Eschka mixture is permissible only when the crucibles are heated in a muffle.

8.2.1 Open Flame—Heat the crucible, placed in a slanting position on a triangle, over a very low flame to avoid rapid expulsion of the volatile matter that tends to prevent complete absorption of the products of combustion of the sulfur. Heat the crucible slowly for 30 min, gradually increase the temperature, and occasionally stir until all black particles have disappeared, which is an indication of the completeness of the procedure.

8.2.2 Muffle (Coal)—Place the crucible in a cold-vented muffle and gradually raise the temperature to $800 \pm 25^\circ\text{C}$ in about 1 h. Maintain this maximum temperature until, on stirring, all black particles have disappeared (about $1\frac{1}{2}$ h).

8.2.3 Muffle (Coke)—Place the crucible in a warm-vented muffle (about 200°C) and gradually raise the temperature to $800 \pm 25^\circ\text{C}$ in about 30 min. Maintain this maximum temperature until, on stirring, all black particles have disappeared.

8.3 Subsequent Treatment—Remove the crucible and empty the contents into a 200-mL beaker and digest with 100 mL of hot water for $\frac{1}{2}$ to $\frac{3}{4}$ h, while stirring occasionally. Decant the solution through filter paper, retaining as much insoluble material in beaker as possible. Thoroughly wash the insoluble matter in the beaker with hot water. After several washings in this manner, transfer the insoluble matter to the filter and wash five times with hot water, keeping the mixture well agitated. Make the filtrate, amounting to about 250 mL, just neutral to methyl orange with NaOH or Na_2CO_3 solution; then add 1 mL of HCl (1+9). Boil and add slowly from a pipet, while stirring constantly, 10 mL or more of BaCl_2 solution. The BaCl_2 solution must be in excess. If more than 10 mL of BaCl_2 solution is required, reduce the weight of sample to about 0.5 g and repeat the ignition and digestion. Continue boiling for 15 min and allow to stand for at least 2 h, or preferably overnight, at a temperature just below boiling. Filter through a fine ashless paper, such as Whatman No. 42 or similar, and wash with hot water until 1 drop of silver nitrate (AgNO_3) solution produces no more than a slight opalescence when added to 8 to 10 mL of filtrate.

8.3.1 Place the wet filter containing the precipitate of barium sulfate (BaSO_4) in a weighed platinum, porcelain, silica, or alundum crucible, fold the paper loosely over the precipitate to allow a free access of air but prevent spattering. Smoke the paper off gradually in a muffle furnace and at no time allow to burn with flame. After the paper is practically consumed, raise the temperature to approximately $800 \pm 50^\circ\text{C}$ and heat to constant weight. Weigh the barium sulfate to the nearest 0.1 mg.

8.4 Blanks and Corrections—In all cases, a correction must be applied. The preferred method of correction is by the analysis of a weighed portion of a standard sulfate using the prescribed reagents and operations in full compliance with the standard. It is acceptable but less accurate to make corrections by running a reagent blank in duplicate using procedures exactly as described in Section 9 of the standard, using the same amount of all reagents that were employed in the routine determination. If the standard sulfate analysis procedure is carried out once a week, or whenever a new supply of a reagent is used, for a series of solutions covering the approximate range of sulfur concentrations in the samples, it is only necessary to add to or subtract from the

⁶ "Reagent Chemicals, American Chemical Society Specification," Am. Chem. Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, NY, and the "United States Pharmacopeia."

weight of BaSO_4 determined for the sample, the deficiency or excess found by the appropriate "check" determination. This is more accurate than the simple reagent blank because, for the amounts of sulfur in question and the conditions of precipitation prescribed, the solubility error for BaSO_4 is probably the largest one to be considered. Barium sulfate is soluble in acids and pure water, and the solubility limit is reached almost immediately on contact with the solvent. Hence, if very high-purity reagents are used or extra precaution is exercised, there may be no sulfate apparent in the "blank." In other words, the solubility limit for BaSO_4 has not been reached or, at any rate, not exceeded; consequently, some sulfate in the sample may remain in solution or redissolve.

9. Calculation

9.1 Calculate the sulfur content as follows:

$$\text{Sulfur, \% in the analysis sample} = \frac{(A - B) \times 13.738}{C}$$

where:

- A = grams of BaSO_4 precipitated,
- B = grams of BaSO_4 correction, and
- C = grams of sample used.

METHOD B—BOMB WASHING METHOD¹

10. Reagents

10.1 Purity of Reagents—(See 7.1.)

10.2 Purity of Water—(See 7.2.)

10.3 Ammonium Hydroxide (sp gr 0.90)—Concentrated ammonium hydroxide (NH_4OH).

10.4 Hydrochloric Acid (1+1)—(See 7.5.)

10.5 Sodium Carbonate Solution—Dissolve 20.90 g of anhydrous sodium carbonate (Na_2CO_3) in water and dilute to 1 L. The Na_2CO_3 should be previously dried for 24 h at 105°C.

10.6 Wash Solution—Dilute 1 mL of a saturated solution of methyl orange to 1 L with water.

11. Procedure

11.1 Ignition—Sulfur is determined in the washings from the oxygen-bomb calorimeter following the calorimetric determination (Test Method D 2015). The type of bomb, amount of water in the bomb, oxygen pressure, and amount of sample taken shall be the same as specified in the calorimetric determination (Test Method D 2015). The bomb shall stand in the calorimeter water for not less than 5 min after firing.

11.1.1 Caution—The following precautions are recommended for safe calorimeter operation. Additional precautions are given in Recommended Practice E 144.

11.1.1.1 The weight of coal or coke sample and the pressure of the oxygen admitted to the bomb must not exceed the bomb manufacturer's recommendations.

11.1.1.2 Carefully inspect bomb parts after each use. Frequently check the threads on the main closure for wear. Replace cracked or significantly worn parts. Return the bomb to the manufacturer occasionally for inspection and possibly proof firing.

11.1.1.3 Equip the oxygen supply cylinder with an approved type of safety device, such as a reducing valve, in addition to the needle valve and pressure gage used in regulating the oxygen feed to the bomb. Valves, gages, and gaskets must meet industry safety code. Suitable reducing valves and adaptors for 300 to 500-psi (2070 to 3440 KPa) discharge pressure are obtainable from commercial sources of compressed gas equipment. Check the pressure gage periodically for accuracy.

11.1.1.4 During ignition of a sample, the operator must not permit any portion of his body to extend over the calorimeter.

11.1.1.5 Exercise extreme caution when combustion aids are employed so as not to exceed the bomb manufacturer's recommendations and to avoid damage to the bomb. Do not fire loose fluffy material, such as unpelleted benzoic acid, unless thoroughly mixed with the sample.

11.1.1.6 Admit oxygen slowly into the bomb so as not to blow powdered material from the crucible.

11.1.1.7 Do not fire the bomb if it has been filled to greater than 30 atm (3 MPa) pressure with oxygen, the bomb has been dropped or turned over after loading, or there is evidence of a gas leak when the bomb is submerged in the calorimeter water.

11.2 Subsequent Treatment—Remove the bomb from the calorimeter water and open the valve carefully so as to allow the gases to escape at an approximately even rate so the pressure is reduced to atmospheric in not less than 1 min. Bombs equipped with valves other than needle valves, such as compression valves, shall be provided with a device so the valve can be controlled to permit a slow and uniform release of the gases. Open the bomb and examine the inside for traces of unburned material or sooty deposit. If these are found, discard the determination. Wash carefully all parts of the interior of the bomb, including the capsule, with a fine jet of water containing methyl orange (10.6) until no acid reaction is observed. It is essential to wash through the valve opening in the case of bombs equipped with compression valves, or other types of valves with large openings, as considerable spray may collect in such valve openings.

11.3 Collect the washings in a 250-mL beaker and titrate with standard sodium carbonate solution (10.5) to obtain the "acid correction" for the heating value, as specified under the calorimetric determination Test Method D 2015. Adjust the pH from 5.5 to 7.0 with dilute NH_4OH , heat the solution to boiling, and filter through a qualitative paper. Wash the residue and paper thoroughly five or six times with hot water. Adjust the acidity of the filtrate and washings, amounting to about 250 mL, precipitate, and determine the sulfur as specified under the Eschka method, Sections 6 through 9, inclusive. Begin analysis at Section 8.

NOTE 2—If the use of 1-g sample weight in the calorimetric determination produces an excess amount of sulfate that can be precipitated by the addition of 10 mL of barium chloride solution, either of the following alternatives may be used: (1) increase the amount of the barium chloride solution from 10 mL in increments of 5 mL up to a maximum of 20 mL of solution, or (2) reduce the amount of sample

¹ Journal of the American Chemical Society, JACSA, Vol 32, 1910, p. 588; Vol 33, 1911, p. 829.

² Selvig, W. A., and Fieldner, A. C. "Check Determinations of Sulfur in Coal and Coke by the Eschka, Bomb-Washing and Sodium Peroxide Fusion Methods." Industrial and Engineering Chemistry: JECHEA, Vol 29, 1927, pp. 729-733.

from 1 to 0.5 g and add 0.5 g of benzoic acid in order to maintain appropriate temperature rise so the precision of the gross calorific value determination is not adversely affected.

12. Report

12.1 The percentage sulfur value obtained using any of the described methods is on an as-determined basis.

12.2 The results of the sulfur analysis may be reported on any of a number of bases, differing from each other in the manner by which moisture is treated.

12.3 Use the percentage of moisture as determined by Test Method D 3173 to calculate the as-determined results from the analysis basis to a dry basis.

12.4 Procedures for converting the value obtained on the analysis sample to other bases are described in Methods D 3176 and D 3180.

13. Precision and Bias

13.1 *Repeatability*—Results of two consecutive determinations carried out on the same sample in the same

laboratory by the same operator using the same apparatus should not differ more than the following in more than 5 of 100 instances:

	%
Coal containing less than 2 % sulfur	0.05
Coal containing 2 % sulfur or more	0.10
Coke	0.03

13.2 *Reproducibility*—The means of results of duplicate determinations carried out by different laboratories on representative samples taken from the same bulk sample after the last stage of reduction should not differ by more than the following in more than 5 of 100 instances:

	%
Coal containing less than 2 % sulfur	0.10
Coal containing 2 % sulfur or more	0.20
Coke	0.05

13.3 *Bias*—These are stoichiometric methods that agree with each other very well when known amounts of solutions or compounds containing predetermined quantities of sulfur (preferably as sulfate) are added to blanks determined as described in 8.4.

The American Society for Testing and Materials takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, 1916 Race St., Philadelphia, PA 19103.



Standard Test Methods for Carbon and Hydrogen in the Analysis Sample of Coal and Coke¹

This standard is issued under the fixed designation D 3178; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 These test methods cover the determination of total carbon and hydrogen in samples of coal or coke. Both the carbon and hydrogen are determined in one operation. This test method yields the total percentages of carbon and hydrogen in the coal as analyzed and the results include not only the carbon and hydrogen in the organic matter, but also the carbon present in mineral carbonates and the hydrogen present in the free moisture accompanying the sample as well as hydrogen present as water of hydration of silicates.

NOTE 1—It is recognized that certain technical applications of the data derived from this test procedure may justify additional corrections. These corrections could involve compensation for the carbon present as carbonates, the hydrogen of free moisture accompanying the sample, and the calculated hydrogen present as water of hydration of silicates.

1.2 When data are converted and reported on the "dry" basis, the hydrogen value is corrected for the hydrogen present in the free moisture accompanying the sample.

1.3 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of whoever uses this standard to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

- 2.1 *ASTM Standards:*
 - D 346 Method of Collection and Preparation of Coke Samples for Laboratory Analysis²
 - D 1193 Specification for Reagent Water³
 - D 2013 Method of Preparing Coal Sample for Analysis²
 - D 3173 Test Method for Moisture in the Analysis Sample of Coal²
 - D 3176 Method for Ultimate Analysis of Coal and Coke²
 - D 3180 Method for Calculating Coal and Coke Analyses from As-Determined to Different Bases²

3. Sample

3.1 The sample shall be the material pulverized to pass No. 60 (250- μ m) sieve and well mixed ~~_____~~

Weigh and record the percent passing through the sieve.

3.2 The test sample should be weighed just prior to commencing the analysis to minimize chance for moisture change. A change in moisture content would introduce error in the hydrogen analysis. In order to provide the data necessary to correct for the hydrogen present in the moisture and ensuing final calculations of both the hydrogen and carbon, a separate sample should be weighed out at the same time for a moisture analysis, and analyzed in accordance with Test Method D 3173.

TOTAL CARBON AND TOTAL HYDROGEN

4. Summary of Method

4.1 The determination of carbon and hydrogen is made by burning a weighed quantity of sample in a closed system and fixing the products of combustion in an absorption train after complete oxidation and purification from interfering substances. This test method gives the total percent of carbon and hydrogen in the coal as analyzed, and includes the carbon in carbonates and the hydrogen in the moisture and in the water of hydration of silicates.

5. Significance and Use

5.1 Carbon and hydrogen values are used to calculate the amount of oxygen (air) required in combustion processes, and in the calculations of efficiency of combustion processes.

5.2 Carbon and hydrogen determinations are used in material balances on coal conversion processes; also one or the other is frequently used in correlations of chemical and physical properties, such as yields of products in liquefaction, reactivity in gasification, and the density and porosity of coal.

6. Apparatus

6.1 *Oxygen Purifying Train*, consisting of the following units arranged as listed in the order of passage of oxygen:

6.1.1 *First Water Absorber*—A container for the solid dehydrating reagent. It shall be so constructed that the oxygen must pass through a column of reagent adequate to secure water equilibrium equal to that secured in the prescribed absorption train. A container of large volume and long path of oxygen travel through the reagent will be found to be advantageous where many carbon and hydrogen determinations are made.

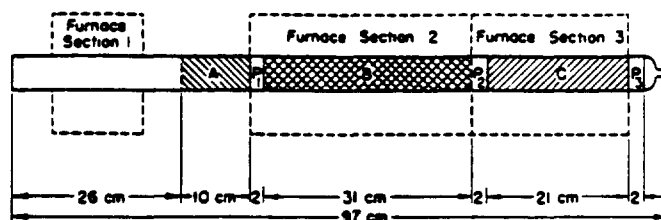
6.1.2 *Carbon Dioxide Absorber*—A container for solid carbon dioxide absorbing agent. It shall be constructed as described in 6.1.1 and shall provide for a column of adequate to remove carbon dioxide completely.

¹ These test methods are under the jurisdiction of ASTM Committee D-5 on Coal and Coke and are the direct responsibility of Subcommittee D05.21 on Methods of Analysis.

Current edition approved March 30, 1984. Published May 1984. Originally published as D 3178-73. Last previous edition D 3178-73 (1979).

² *Annual Book of ASTM Standards*, Vol 05.05.

³ *Annual Book of ASTM Standards*, Vol 11.01.



A—Clear fused quartz section (optional) when a translucent quartz tube is used.
 B—Cupric oxide filling.
 C—Lead chromate or silver filling.
 P₁, P₂, or P₃—oxidized copper gauze plugs.

NOTE—All dimensions are given in centimetres. When furnace sections longer than those specified in 6.3 are to be used, changes in the above dimensions shall be in accordance with the provisions of Note 5.

FIG. 1 Arrangement of Tube Fillings for Combustion Tube

6.1.3 *Second Water Absorber*, same as specified in 6.1.1

6.2 *Flowmeter*, used to permit volumetric measurement of the rate of flow of oxygen during the determination. It shall be suitable for measuring flow rates within the range from 50 to 100 mL/min (standard temperature and pressure). The use of a double-stage pressure-reducing regulator with gage and needle valve preceding the first water absorber is recommended to permit easy and accurate adjustment of the rate of flow.

6.3 *Combustion Unit*—The combustion unit shall consist of three electrically heated furnace sections, individually controlled, which may be mounted on rails for easy movement; the upper part of each furnace may be hinged so that it can be opened for inspection of the combustion tube. The three furnace sections shall be as follows:

6.3.1 *Furnace Section 1*, nearest the oxygen inlet end of the combustion tube, approximately 130-mm long and used to heat the inlet end of the combustion tube and the sample. It shall be capable of rapidly attaining an operating temperature of 850 to 900°C (Note 2).

6.3.2 *Furnace Section 2*, approximately 330 mm in length and used to heat that portion of the tube filled with cupric oxide. The operating temperature shall be $850 \pm 20^\circ\text{C}$ (Note 2).

6.3.3 *Furnace Section 3*, approximately 230 mm-long, and used to heat that portion of the tube filled with lead chromate or silver. The operating temperature shall be $500 \pm 50^\circ\text{C}$.

NOTE 2—Combustion tube temperature shall be measured by means of a thermocouple placed immediately adjacent to the tube near the center of the appropriate tube section.

6.3.4 *Combustion Tube*—The combustion tube shall be made of fused quartz or high-silica glass⁵ and shall have a nominal inside diameter which may vary within the limits of 19 to 22 mm and a minimum total length of 970 mm. The exit end shall be tapered down to provide a tubulated section for connection to the absorption train. The tubulated section shall have a length of 20 to 25 mm, an internal diameter of not less than 3 mm, and an external diameter of approximately 7 mm. The total length of the reduced end shall not exceed 60 mm. If a translucent fused quartz tube is used, a

transparent section 190-mm long, located 250 mm from the oxygen inlet end of the tube, will be found convenient (see Fig. 1).

6.3.5 *Combustion Boat*—This shall be either glazed porcelain, fused silica, or platinum. Boats with internal dimensions of approximately 70 by 8 by 8 mm have been found convenient.

6.4 *Absorption Train*—The absorption train shall consist of the following units arranged as listed in the order of passage of oxygen:

6.4.1 *Water Absorber*, having a capacity for 45 cm³ of solid reagent and a minimum length of gas travel through the reagent of 80 mm.⁶

6.4.2 *Carbon Dioxide Absorber*—If solid reagents are used for carbon dioxide absorption the container shall be as described in 6.4.1. If a solution is used, the container shall be a Vanier bulb.

6.4.3 *Guard Tube*—A container as described in 6.4.1.

7. Reagents

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.⁶ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean Type IV reagent water, conforming to Specification D 1193.

7.3 *Oxygen*, 99.5 % purity or better (Note 6).

7.4 *Combustion Tube Reagents*:

7.4.1 *Cupric Oxide* (CuO), wire form, dust-free.

7.4.2 *Fused Lead Chromate*, (PbCrO₄) approximately 2.38 to 0.84 mm size.

⁵ Glass-stoppered containers such as the Nesbitt, Schwartz U-tube and the Stetser-Norton bulbs have been found satisfactory.

⁶ "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Ross, D. Van Nostrand Co., Inc., New York, NY, and the "United States Pharmacopeia."

⁴ Vycor has been found satisfactory for this purpose.

7.4.3 *Silver Gauze*, 99.9 % silver minimum purity, 0.84 mm. made from approximately No. 27 B&S gage wire.

7.4.4 *Copper Gauze*, 99.0 % copper minimum purity, 0.84 mm made from approximately No. 26 B&S gage wire.

7.5 *Purification and Absorption Train Reagents:*

7.5.1 *Water Absorbent*—Anhydrous magnesium perchlorate ($Mg(ClO_4)_2$) of approximately 2.38 to 0.35 mm size.

NOTE 3—Trade names of the reagents are Anhydron and Dehydrite.

7.5.2 *Carbon Dioxide Absorbent*—If a solid reagent is used, it shall be sodium or potassium hydroxide (NaOH or KOH) impregnated in an inert carrier of approximately 2.38 to 0.84 mm size. Use of soda lime in place of the above or in admixture with them is permissible (Note 4). If a solution is used, it shall be 30 weight % potassium hydroxide (KOH).

NOTE 4—Trade names of the sodium and potassium hydroxide permissible solid carbon dioxide absorbing reagents are: Ascarite, Caroxite, and Mikohbite. If soda lime is used in admixture with any of the foregoing, it should not exceed 30 weight % of the total reagent. In using Ascarite it may be necessary to add a few drops of water to this reagent to assure complete absorption of carbon dioxide.

8. Preparation of Apparatus

8.1 *Combustion Tube Packing*—To ensure complete oxidation of combustion products and complete removal of interfering substances such as oxides of sulfur, the combustion tube shall be packed with cupric oxide and lead chromate or silver. The arrangement and lengths of the tube fillings and separating plugs shall be as shown in Fig. 1. It is recommended that the tube be placed in a vertical position (constricted end downward) for packing. When filling the tube with lead chromate, any residual reagent adhering to the walls of the empty portion of the tube must be removed. When silver is used as a tube filling, the required length of filling may be prepared conveniently from three or four strips of silver gauze 150 to 200-mm long, by rolling each strip into a cylindrical plug and inserting the strips end-to-end in the tube.

NOTE 5—Longer furnaces with appropriate lengths of tube packing will be satisfactory.

8.2 *Absorption Train:*

8.2.1 *Water Absorber*—A container is filled with a permissible solid desiccant by adding the required amount in small portions and settling each portion by gentle tapping between additions. A glass wool plug shall be placed between the reagent and the absorber outlet to prevent loss of reagent "dust".

8.2.2 *Carbon Dioxide Absorber*—If a solid reagent is used for the retention of carbon dioxide, the absorber shall be filled as described in 8.2.1. A layer or "cap" of desiccant shall be placed in the outlet section of the container and shall be the same as that used in the water absorber. This layer shall have a bulk volume not less than one fourth nor more than one third of the combined volume of both reagents. If a liquid absorbent is used, the inner tube of the Vanier bulb shall be filled with the same desiccant used in the water absorber. A glass wool plug shall be placed in the outlet section of the container to prevent loss of reagent "dust".

8.2.3 *Guard Tube*, packed with equal volumes of the water absorbent and a solid carbon dioxide absorbent.

8.2.4 *Connections*—To ensure a closed system from the supply tank of oxygen to the guard tube at the end of the absorption train, it is recommended that all connections by glass-to-glass or glass-to-quartz butt joints with short lengths of flexible tubing as seals. The connection between the purification train and the combustion tube may be made by means of a rubber stopper or other suitable device. All connections shall be gas tight. No lubricant shall be used for making tubing connections in the absorption train.

8.3 *Conditioning of Apparatus:*

8.3.1 *Newly Packed Combustion Tube*—Burn a sample of coal or coke as described in 9.4 except that the products of combustion need not be fixed in a weighed absorption train.

8.3.2 *Used Combustion Tube*—After any extended shut down, one day or more, test the combustion train under procedure conditions, but without burning a sample, for 40 min with weighed absorption bulbs connected. A variation of not more than 0.5 mg of either bulb shall be considered satisfactory.

NOTE 6—If the blank tests for flow indicate interfering impurities in the oxygen supply by consistent weight-gain in the absorption bulbs, eliminate these impurities by using a preheater furnace and tube, filled with cupric oxide. Operate this preheater furnace at $850 \pm 20^\circ C$ and insert in series between the supply tank of oxygen and the purification train.

8.3.3 *Absorption Train*—Condition freshly packed absorber and guard tubes by burning a sample of coal or coke as described in 9.4 except that tube weights need not be determined.

8.3.4 *Standard Checks* shall be made frequently, particularly when intermittent use of the combustion train is common or when any changes have been made in the system. A standard substance of certified analysis, such as benzoic acid or sucrose as furnished by the National Bureau of Standards shall be burned as described in Section 9. A variation from the theoretical of not more than 0.07 % for hydrogen nor more than 0.30 % for carbon shall be considered satisfactory.

9. Procedure

9.1 After the combustion tube and absorbers have been conditioned as prescribed in Section 8, conduct the test as follows:

9.2 *Absorption Train*—Bring the absorption tubes to room temperature near the balance for 15 to 20 min, vent momentarily to the atmosphere, wipe with a chamois or lint-free cloth in the areas where handled, and weigh to the nearest 0.1 mg.

9.3 *Sample*—Weigh approximately 0.2 g (weighed to the nearest 0.1 mg) of air-dry sample ground to pass a No. 60 (250- μm) sieve into a combustion boat.

9.4 *Sample Analysis*—With furnace (6.3.2 and 6.3.3) at specified temperatures and positioned as shown in Fig. 1, perform the following operations in rapid succession in the order listed:

9.4.1 If a conventional type of sample heating furnace is used for heating (6.3.1), place it so that its left-hand edge is about 100 mm from the oxygen inlet end of the combustion tube.

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where:

9.4.2 Attach the weighed absorption train to the tube:
9.4.3 Push the sample boat into the tube to a point within approximately 20 mm from plug P_1 ;

9.4.4 Close the tube and adjust the oxygen flow to a rate of 50 to 100 mL/min (standard temperature and pressure) being the same as used in blanking (see 8.3.2).

9.4.5 Apply full heat to heating section No. 1 to bring it to an operating temperature of 850 to 900°C as rapidly as possible. Move the heater slowly toward the boat so that it completely covers the boat and is brought into contact with heating (6.3.2) in a period of 10 to 20 min (Note 7). Allow it to remain in this position for an additional 5 to 10 min and then shut off the heat and return the sample heater to its original position. Continue to the flow of oxygen through the tube for 10 min (Note 8), close the absorbers under a positive pressure of oxygen, and detach them from the train. Remove the absorbers to the vicinity of the balance, allow them to cool to room temperature for 15 to 20 min, vent momentarily to atmosphere, wipe them with a chamois or lint-free cloth in the areas handled, and finally weigh them to the nearest 0.1 mg. While the absorbers are cooling, it is recommended that the ash remaining in the combustion boat be examined for traces of unburned carbon which, if present, will nullify the determination.

NOTE 7—Some variation in operating technique and heater manipulation may be permitted here at the discretion of the analyst, provided that it is conducive to a gradual and controlled release of volatile matter. Conditions that lead to visible burning (flame combustion) of the sample shall be avoided.

NOTE 8—Since water may condense in the cooler outlet end of the combustion tube or in the inlet arm of the water absorber, the use of an external or internal heat conducting device (a metal heat bridge) is recommended to prevent such condensation or promote reevaporation during this flushing period.

10. Calculations

10.1 Calculate the percentage of carbon (Note 9) in the analysis sample as follows:

$$\text{Carbon, \%} = (A \times 27.289)/B$$

where:

A = increase in weight of CO_2 absorption bulb, g, and
 B = grams of sample used.

NOTE 9—It is recognized that formation of oxides of nitrogen during the combustion procedure may lead to slightly high results for carbon. However, extensive study of this effect by five laboratories led to the conclusion that error so incurred would not be significant in commercial application. In certain research applications, where accuracy of a higher order is required, means of removing oxides of nitrogen prior to water and carbon dioxide absorption should be included.

10.2 *Hydrogen*—Calculate the percentage of hydrogen in the analysis sample (Note 10) as follows:

$$\text{Hydrogen, \%} = (C \times 11.19)/B$$

where:

B = grams of sample used, and
 C = increase of weight of water absorption bulb, g.

NOTE 10—The water absorbed in the water absorption tube includes not only water formed as a product of combustion, but also free water (moisture) in the sample and water of hydration of any clay minerals present.

11. Report

11.1 The results of the carbon and hydrogen analysis may be reported on any of a number of bases, differing from each other in the manner by which moisture is treated.

11.2 Use the percentage of moisture in the sample passing a No. 60 (250- μm) sieve to calculate the results of the analysis sample to a dry basis.

11.3 Procedures for converting the values obtained on the analysis sample to other bases are described in Methods D 3176 and D 3180.

12. Precision and Bias

12.1 The permissible differences between two or more determinations shall not exceed the following values:

	Repeatability, %	Reproducibility, %
Carbon	0.3	...
Hydrogen	0.07	...

12.2 The bias of this test method cannot be determined at this time.

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Standard Test Methods for Nitrogen in the Analysis Sample of Coal and Coke¹

This standard is issued under the fixed designation D 3179; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 These test methods cover the determination of total nitrogen in samples of coal and coke. The analytical data from these test methods are to be reported as part of ultimate analysis where ultimate analysis is requested. If ultimate analysis is not requested, the value is to be reported according to the request. Two methods are included as follows:

	Sections
Method A—Kjeldahl-Gunning Macro Analysis, with an alternative technique included	9 to 16
Method B—Kjeldahl-Gunning Semi-Micro Determination	17 to 23

1.2 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of whoever uses this standard to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

- 2.1 *ASTM Standards:*
 D 121 Definitions of Terms Relating to Coal and Coke²
 D 346 Method of Collection and Preparation of Coke Samples for Laboratory Analysis²
 D 1193 Specification for Reagent Water³
 D 2013 Method of Preparing Coal Samples for Analysis²
 D 3173 Test Method for Moisture in the Analysis Sample of Coal and Coke²
 D 3176 Method for Ultimate Analysis of Coal and Coke²
 D 3180 Method for Calculating Coal and Coke Analyses from As-Determined to Different Bases²
 E 380 Metric Practice⁴

3. Summary of Methods

3.1 In these procedures, nitrogen is converted into ammonium salts by destructive digestion of the sample with a hot, catalyzed mixture of concentrated sulfuric acid and potassium sulfate. These salts are subsequently decomposed in a hot alkaline solution from which the ammonia is recovered by distillation and finally determined by alkalimetric or acidimetric titration.

¹ These test methods are under the jurisdiction of ASTM Committee D-5 on Coal and Coke and are the direct responsibility of Subcommittee D05.21 on Methods of Analysis.

Current edition approved March 30, 1984. Published May 1984. Originally published as D 3179-73. Last previous edition D 3179-73 (1979).

² Annual Book of ASTM Standards, Vol 05.05.

³ Annual Book of ASTM Standards, Vol 11.01.

⁴ Annual Book of ASTM Standards, Vol 14.02. Excerpts appear in the gray pages of all the volumes.

4. Significance and Use

4.1 Nitrogen results obtained by these test methods are required to fulfill the requirements of the ultimate analysis, Test Method D 3173. Also, results obtained may be used to evaluate the potential formation of nitrogen oxides as a source of atmospheric pollution.

4.2 Nitrogen data are used in comparing coals and in research. When the oxygen content of coal is estimated by difference, it is necessary to make a nitrogen determination.

5. Definitions

5.1 For definitions of terms used in these test methods, refer to Definitions D 121. For an explanation of the metric system including units, symbols, and conversion factors, see Standard E 380.

6. Interferences

6.1 No significant interferences have been determined using these procedures. However, strict adherence is necessary when using these nitrogen procedures to obtain reproducible results.

7. Reagents

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.⁵ Other grades may be used, provided it is first ascertained that the reagent is of sufficient purity to meet its use without lessening the accuracy of the determination.

7.2 *Water*—Unless otherwise indicated, references to water shall be understood to mean Type II reagent water, conforming to Specification D 1193.

8. Sampling and Preparation

8.1 The sample shall be the material pulverized to pass No. 60 (250- μ m) sieve. Weigh and record the percent passing through the sieve.

8.2 A separate portion of the analysis sample should be analyzed for moisture content in accordance with Test Method D 3173, in order to allow calculation of the as-analyzed data to other bases.

⁵ "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, DC. For suggestions on the testing of reagents not in the American Chemical Society, see "Reagent Chemicals and Standards," Joseph Rosin, D. Van Nostrand Co., Inc., New York, NY, and the "United States Pharmacopeia."

METHOD A—MACRO-NITROGEN DETERMINATION WITH ALTERNATIVE METHOD INCLUDED

9. Scope and Application

9.1 This test method describes a macro procedure for the determination of nitrogen in both coal and coke, by two alternative procedures. In both procedures, a 1 g sample is digested with a hot catalyzed mixture of concentrated sulfuric acid and potassium sulfate, which converts the nitrogenous compounds to ammonium salts. The salts are then decomposed in a hot alkaline solution, releasing the ammonia, which is then distilled into either standard sulfuric-acid or boric-acid solution and finally determined by alkalimetric or acidimetric titration.

10. Apparatus

10.1 *Digestion Unit*—An electrically heated digestion rack or a gas burner; either type of heater shall be provided with adequate means of control to maintain digestion rates as described in 12.1. It is essential that an electric digestion rack provides adjustable controls to regulate desirable digestion temperatures. To eliminate emission of sulfur-acid fumes, the digestion process must be carried out under a well-ventilated fume hood. Commercially made multiple-unit digestion racks provided with fume exhaust ducts may be used.

10.2 *Digestion Flasks*—Made of heat-resistant glass,⁶ having a capacity of 500 or 800 mL.

10.3 *Distillation Unit*—A suitable glass steam distillation unit with a splash head to trap any entrained caustic soda and also provided with adequate means of control to maintain distillation rates as described in 12.1. Commercially made multiple unit distillation racks provided with water-cooled glass or block-tin condensers may be used.

10.4 *Buret*—Microburet graduated in 0.01 mL. A 50 mL microburet is needed for Method A.

10.5 *Erlenmeyer Flask*—Having a capacity of 250 to 300 mL.

10.6 *Rubber Tubing*—Sufficient for attaching condenser to cooling water supply and drain.

10.7 *Pipets*—As required.

11. Reagents

11.1 *Alkali Solution*—Dissolve 8.0 g of potassium sulfide (K_2S) and 500 g of sodium hydroxide ($NaOH$) (Caution-Hazard) in water and dilute to 1 L. The use of appropriate amounts of sodium sulfide (Na_2S) or potassium hydroxide (KOH) may be substituted (Note 1(3)).

11.2 *Ethyl Alcohol (95 %)*—Ethyl alcohol conforming to Formula No. 30 or 2A of the U.S. Bureau of Internal Revenue. Methyl alcohol may be used.

11.3 *Mercury*.

NOTE 1—Other satisfactory and permissible catalysts for the digestion, together with the quantities of K_2SO_4 required in their use are as follows:

(1) Five grams of a mixture containing 32 parts by weight of K_2SO_4 , 5 parts by weight of mercuric sulfate ($HgSO_4$), and one part by weight of selenium.

(2) Three-tenths gram of mercuric selenite ($HgSeO_3$) with 7 to 10 g of K_2SO_4 .

(3) Three-tenths gram of cupric selenite dihydrate ($CuSeO_3 \cdot 2H_2O$) with 7 to 10 g of K_2SO_4 . When this mixture is used, the addition of a sulfide to the alkali solution is not necessary.

11.4 *Potassium Permanganate* ($KMnO_4$), crystals.

11.5 *Potassium Sulfate* (K_2SO_4), crystals.

11.6 *Sucrose*, National Bureau of Standards primary-standard grade.

11.7 *Sulfuric Acid* (sp gr 1.84)—Concentrated sulfuric acid (H_2SO_4) (Caution-Hazard).

11.8 *Zinc*, mossy or granular.

REAGENTS REQUIRED ONLY FOR KJELDAHL-GUNNING METHOD

11.9 *Methyl Red Indicator Solution* (0.4 to 1 g/L)—Dissolve 0.04 to 0.1 g of methyl red in 50 mL of 95 % ethyl alcohol or methyl alcohol and add 50 mL of water. Bromocresol green solutions to equal concentrations may be used.

11.10 *Sodium Hydroxide, Standard Solution* (0.1 to 0.2 N)—Prepare and accurately standardize a 0.1 to 0.2 N sodium hydroxide ($NaOH$) solution against a primary standard.

11.11 *Sulfuric Acid* (0.2 N)—Prepare and standardize a 0.2 N sulfuric acid (H_2SO_4) solution. The solution need not be standardized against a primary standard.

REAGENTS REQUIRED ONLY FOR ALTERNATIVE METHOD

11.12 *Boric Acid Solution* (50 g/L)—Dissolve 5 g of boric acid (H_3BO_3) in 100 mL of boiling water. Allow to cool before use.

11.13 *Mixed Indicator Solution*—Prepare a solution containing 0.125 % methyl red and 0.083 % methylene blue in 95 % ethyl alcohol or in methyl alcohol. Prepare a fresh solution at bimonthly intervals.

11.14 *Sulfuric Acid* (0.1 to 0.2 N)—Prepare and accurately standardize a 0.1 to 0.2 N sulfuric acid (H_2SO_4) solution against a primary standard; hydrochloric acid (HCl) of similar concentration may be substituted.

12. Procedure

12.1 Weigh approximately 1 g (weighed to nearest 1 mg) of the analysis sample and carefully transfer into a 500 or 800-mL Kjeldahl flask containing 7 to 10 g of K_2SO_4 and 0.6 to 0.8 of mercury (Note 1). Add 30 mL of H_2SO_4 (sp gr 1.84) to the mixture by pouring down the neck of the flask with rotation, in order to wash any adherent sample material into the mixture. Swirl the contents of the flask several times to ensure thorough mixing and wetting of the sample. Incline the flask at an angle of 45 to 60° on the digestion heater in a fume hood (Note 2), and heat the contents to boiling; controlling the heat so the H_2SO_4 vapors condense no more than halfway up the neck of the flask. Continue the boiling until all sample particles are oxidized, as evidenced by a nearly colorless solution, or for at least 2 h after the solution has reached a straw-colored stage. The total time of digestion will require 6 h.

When the digestion is completed and the solution has cooled, a few crystals of $KMnO_4$ are added to ensure complete

⁶ Borosilicate glass has been found satisfactory for this purpose.

oxidation; further heating may be necessary to destroy the excess permanganate and decolorize the solution.

NOTE 2—When fume exhaust ducts or hoods are not available, a Hengar tube may be inserted in the neck of the flask.

NOTE 3—Addition of 0.1 g of chromic trioxide (CrO_3) to the digestion mixture has been found very helpful in reducing the time of digestion for coke.

12.2 Dilute the cooled digestion mixture to about 300 mL with cold water, and remove any heat of dilution by cooling with water. Meanwhile, pipet into the 250 or 300-mL Erlenmeyer flask, 20.0 mL of 0.2 N H_2SO_4 and add 6 drops of methyl red or bromocresol green indicator solution. Attach the glass connecting tube to the discharge end of the condenser, using the short piece of rubber tubing as a seal. Incline the Erlenmeyer flask at a suitable angle, and insert this tube so that the end is immersed to the maximum depth in the acid. Add 1 to 2 g of granular zinc to the mixture in the Kjeldahl flask (two or three small pieces of mossy zinc is used), and slowly add 100 mL of the alkali solution so that it forms a distinct layer under the acid solution (Caution—Hazard). This may be accomplished by inclining the flask at an angle of 45 to 60° and pouring the alkali solution down the neck. Failure to maintain discrete layers during this operation may lead to loss of ammonia. Quickly connect the flask to the distilling condenser through the Kjeldahl connecting bulb, and then swirl the contents to promote thorough mixing.

12.3 Bring the contents of the Kjeldahl flask to a boil carefully, in order to avoid violent bumping, and then distill the ammonia over into the acid solution in the Erlenmeyer flask. Continue the distillation at a maximum rate of approximately 350 mL/h until 150 to 175 mL of distillate have been collected. Discontinue the boiling, and remove the glass connecting tube from the condenser and Erlenmeyer flask. Rinse the tube with distilled water, collecting the washings in the Erlenmeyer flask, and then back-titrate the excess acid with 0.1 to 0.2 N NaOH solution.

12.4 Run a blank determination in the same manner as described in 12.1 to 12.3 using approximately 1 g of sucrose (weighed to the nearest 1 mg) as the sample material.

NOTE 4—Blank determinations must be made to correct for nitrogen from sources other than the sample. A blank determination shall be made whenever a new batch of any one reagent is used in the analysis.

13. Calculation and Reporting

13.1 Calculate the percentage of nitrogen in the analysis sample as follows:

$$\text{Nitrogen, \%} = (B - A)N \times 0.014/C \times 100$$

where:

- A = millilitres of NaOH solution required for titration of the sample,
 B = millilitres of NaOH solution required for titration of the blank,
 N = normality of the NaOH solution, and
 C = grams of sample used.

14. Procedure for Alternative Technique

- 14.1 Digest the sample as described in 12.1.
 14.2 Dilute and cool the digestion mixture as described in 12.2. Add to the 250 or 300-mL Erlenmeyer flask approxi-

ately 20 mL of H_3BO_3 solution and 5 drops of mixed indicator solution. Then proceed as described in the remainder of 12.2.

14.3 Distill the ammonia into the H_3BO_3 solution exactly as described in 12.3 and finally titrate the ammonia with 0.2 N H_2SO_4 .

14.4 Run a blank determination in the same manner as described in 14.1 to 14.3, using approximately 1 g (weighed to the nearest 1 mg) of sucrose as the sample material (Note 4).

14.5 Calculation—Calculate the percentage of nitrogen in the sample as follows:

Nitrogen, %, in the analysis sample = $(A - B)N \times 0.014/C \times 100$ where:

- A = millilitres of H_2SO_4 required for titration of the sample,
 B = millilitres of H_2SO_4 required for titration of the blank,
 N = normality of the H_2SO_4 , and
 C = grams of the sample used.

15. Report

15.1 The results of the nitrogen analysis may be reported on any of a number of bases, differing from each other in the manner by which moisture is treated.

15.2 Use the percentage of moisture in the sample passing a No. 60 (250- μm) sieve to calculate the results of the analysis sample to a dry basis.

15.3 Procedures for converting the value obtained on the analysis sample to other bases are described in Methods D 3176 and D 3180.

16. Precision and Bias

16.1 The permissible differences between duplicate determinations shall not exceed the following values in more than 5 of 100 instances.

Nitrogen	Repeatability, %	Reproducibility, %
	To be determined	

16.2 The bias of this test method cannot be determined at this time.

METHOD B—KJELDAHL-GUNNING SEMI-MICRO NITROGEN DETERMINATION

17. Scope and Application

17.1 The semi-micro test method differs primarily from the macro-methods in that smaller sized equipment is used. Smaller samples are analyzed (0.1 g compared with a 1.0-g sample for the macro-methods), and ammonia is separated from the alkalized digestion mixture by steam distillation. The same catalysts may be used, although it is more common to use a mixed catalyst in this test method. The acid-base finish may be used, but the boric acid finish is more common.

18. Apparatus

18.1 Digestion Unit—An electrically heated digestion rack with adequate means of control to maintain digestion rates as described in 20.3 on which the digestion flasks may be supported at about a 35° angle.

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18.6
18.7

19. Reagents

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19.5
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saturatec
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the form
NaOH a
liquid.
19.6
19.7
($\text{C}_6\text{H}_{12}\text{N}$
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(Caution
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19.10
19.11
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primar
tration n

20. Procedure

20.1
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of the flas
add 5.0 n
20.3
contents
water. Gr
bumping
slow temp
rati
absence o
digestion



Standard Test Method for Ash in the Analysis Sample of Coal and Coke From Coal¹

This standard is issued under the fixed designation D 3174; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This method covers the determination of the inorganic residue as ash in the analysis sample of coal or coke as prepared in accordance with Method D 2013 or Method D 346. The results obtained can be applied as the ash in the proximate analysis, Method D 3172, and in the ultimate analysis, Method D 3176. For the determination of the constituents in ash, reference is made to Test Methods D 2795 and D 3682. See Definitions D 121 for definition of ash.

2. Referenced Documents

2.1 ASTM Standards:

- D 121 Definitions of Terms Relating to Coal and Coke²
- D 346 Method of Collection and Preparation of Coke Samples for Laboratory Analysis²
- D 388 Classification of Coals by Rank²
- D 1756 Test Method for Carbon Dioxide in Coal²
- D 1757 Test Methods for Sulfur in Ash from Coal and Coke²
- D 2013 Method of Preparing Coal Samples for Analysis²
- D 2795 Test Methods for Analysis of Coal and Coke Ash²
- D 3172 Method for Proximate Analysis of Coal and Coke²
- D 3173 Test Method for Moisture in the Analysis Sample of Coal and Coke²
- D 3176 Method for Ultimate Analysis of Coal and Coke²
- D 3180 Method for Calculating Coal and Coke Analyses from As-Determined to Different Bases²
- D 3682 Test Method for Major and Minor Elements in Coal and Coke Ash by Atomic Absorption²

3. Summary of Method

3.1 Ash is determined by weighing the residue remaining after burning the coal or coke under rigidly controlled conditions of sample weight, temperature, time, atmosphere, and equipment specifications.

4. Significance and Use

4.1 Ash, as determined by this method, is the residue remaining after burning the coal and coke. Ash obtained differs in composition from the inorganic constituents present in the original coal. Incineration causes an expulsion of all water, the loss of carbon dioxide from carbonates, the conversion of iron pyrites into ferric oxide, and other

chemical reactions. Ash, as determined by this method, will differ in amount from ash produced in furnace operations and other firing systems because incineration conditions influence the chemistry and amount of the ash. References for correcting ash results determined by this method to a mineral-matter-free basis are listed in Method D 388, Section 8, Classification of Coal by Rank.

5. Apparatus

5.1 *Electric Muffle Furnace for Coal or Coke* (Note 1)—For determination of ash of coal, the furnace shall have an adequate air circulation and be capable of having its temperature regulated at 700 to 750°C. The furnace shall be equipped with a temperature indicator and means of controlling the temperature within prescribed limits. Means shall be provided for maintaining air flow at a rate of 2 to 4 changes per minute (see Figs. 1 and 2). Inlet and outlet ports shall be located and arranged to distribute the air uniformly throughout the furnace area without the possibility of sweeping solid particles from the capsules. The temperature over the entire working area of the furnace floor shall be maintained within the specified temperature limits.

NOTE 1—Combustion gases shall be vented from laboratory.

5.2 *Porcelain Capsules*, about $\frac{7}{8}$ in. (22 mm) in depth, and $1\frac{1}{4}$ in. (44 mm) in diameter, or similar shallow dishes or platinum crucibles.

5.3 *Balance*, sensitive to 0.1 mg.

5.4 *Crucible Cover*, aluminum, porcelain, or similar covers.

6. Temperature Calibration

6.1 Place a preignited capsule with 1 g of sand at the center of the working area of the furnace, and by the use of a potentiometer and thermocouple or other suitable temperature measuring device measure the temperature of the sand in the crucible. The crucible and sand should be at temperature equilibrium with the furnace. There should be 2 to 4 air changes per minute moving throughout the furnace (the air flow may be measured by using a wet-test meter or equivalent calibrated at standard conditions for air connected to the ceramic-pipe exhaust). Adjust the furnace temperature until the potentiometer reads 750°C \pm 10 and then adjust or read the temperature on the indicating pyrometer. Use this reading as the proper setting for controlling the furnace.

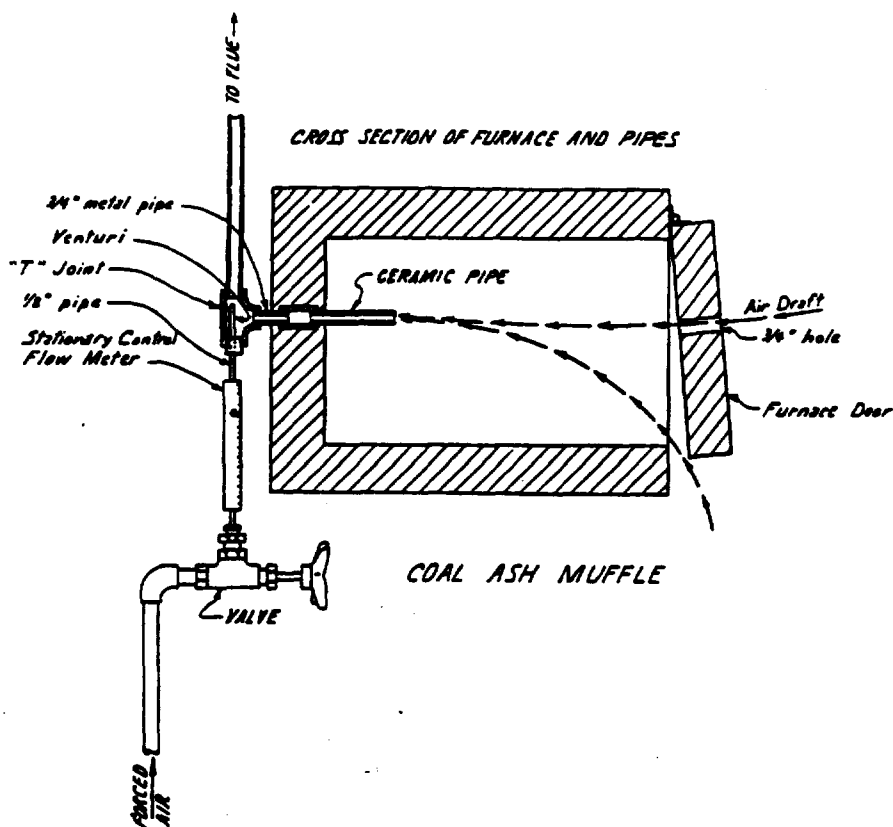
7. Procedure

7.1 Transfer approximately 1 g (weighed to the nearest 0.1 mg) of the thoroughly mixed sample (Note 2) to a weighed capsule and cover quickly. An alternative way is to use the

¹ This method is under the jurisdiction of ASTM Committee D-5 on Coal and Coke and is the direct responsibility of Subcommittee D05.21 on Methods of Analysis.

Current edition approved March 3, 1982. Published May 1982. Originally published as D 3174 - 73. Last previous edition D 3174-73 (1979).

² Annual Book of ASTM Standards, Vol 05.05.



(Suggested method for inducing regulated air flow through ashing furnace.)

FIG. 1 Air Aspirator

dried coal from the moisture determination in Test Method D 3173. Place the capsule containing the sample in a cold furnace and heat gradually at such a rate that the temperature reaches 450 to 500°C in 1 h.

NOTE 2—The sample shall be the material pulverized to pass No. 60 (250-μm) sieve in accordance with Method D 2013 or Method D 346.

7.2 Continue heating so that a temperature of 700 to 750°C is reached by the end of the second hour. Continue the ashing at 700 to 750°C for two additional hours (Note 3). Remove the capsule from the muffle, place the cover on the capsule, cool under conditions to minimize moisture pickup, and weigh.

NOTE 3—While the 4-h incineration interval described is sufficient with most coals to reach a condition of complete burn-off, certain coals and nonreactive coals may require additional time. If unburned carbon particles are observed, or if duplicate results are suspect, the samples should be returned to the furnace for sufficient time to reach a constant weight (± 0.001 g). By this means, pyritic sulfur will be oxidized and expelled before the calcite is decomposed. An ample supply of air in the muffle, "2 to 4 changes per minute," must be assured at all times to ensure complete oxidation of the pyritic sulfur and to remove the SO₂ formed. The 4-h time limit may be reduced if the sample reaches a constant weight at 700 to 750°C in less than 4 h.

NOTE 4—Some samples may be encountered that contain a high amount of carbonates (calcite) or pyrites, or both. In such cases sulfur

retained as sulfates may be both unduly high and nonuniform between duplicate samples. In such cases sulfate sulfur in the ash can be determined in accordance with Test Methods D 1757 and the value properly corrected. If such is done, the ash value should be reported and designated both as determined and corrected.

8. Calculations

8.1 Calculate the ash percent in the analysis sample as follows:

$$\text{Ash in analysis sample, \%} = [(A - B)/C] \times 100$$

where:

- A = weight of capsule, cover, and ash residue, g,
- B = weight of empty capsule and cover, g, and
- C = weight of analysis sample used, g.

9. Report

9.1 For reporting analyses to other than as-determined basis, refer to Method D 3180.

10. Precision

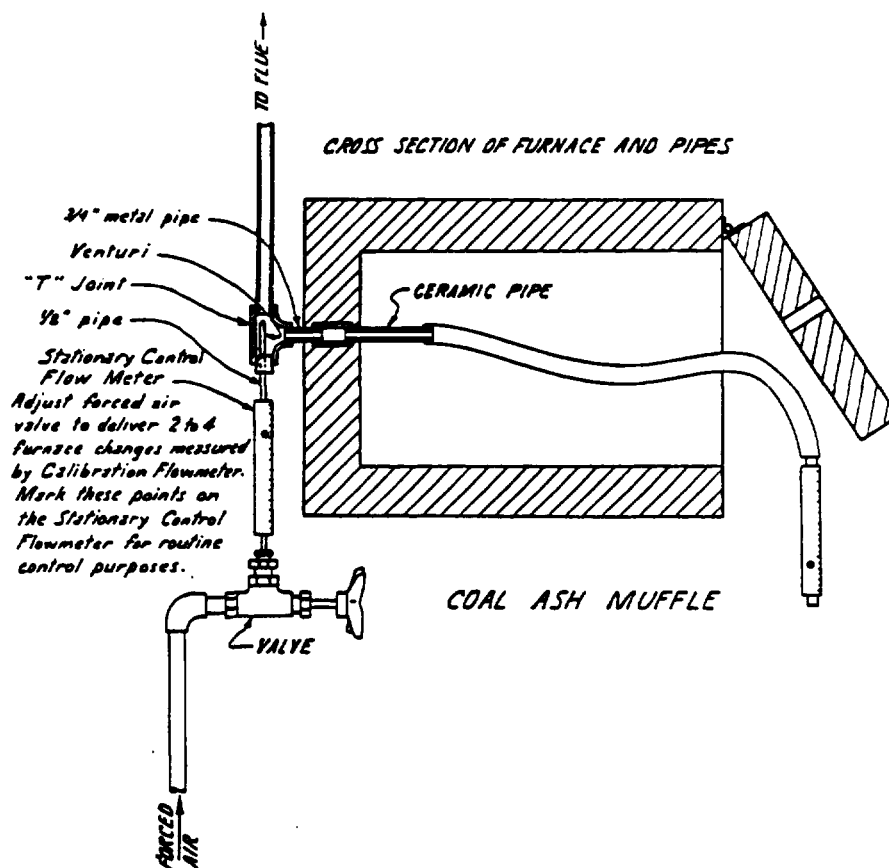
10.1 The following criteria should be used for judging the acceptability of the results:

10.1.1 *Repeatability*—Duplicate results by the same laboratory should not be considered suspect unless they differ by more than the following percentages:

Calibrator
temperature
NOTE—Fk

No car
Carbon:
Coals +
pyrite

10.1.2
more lab



Calibration Flowmeter with Tubing—Ambient Air—For calibration use only, adjust forced air valve to deliver 2 to 4 furnace volume changes per minute (at standard temperature-pressure conditions.)

Note—Flowmeters are usually calibrated for one atmosphere at 70°F (760 mm Hg at 21.1°C).
(Suggested layout for calibration.)

FIG. 2 Air Aspirator

No carbonates present
Carbonates present
Coals with more than 12 % ash containing carbonates and pyrites

0.2 %
0.3 %
0.5 %

they differ by more than the following percentages:

No carbonates present 0.3 %
Carbonates present 0.5 %
Coals with more than 12 % ash containing carbonates and pyrites 1.0 %

10.1.2 Reproducibility—Results submitted by two or more laboratories should not be considered suspect unless

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This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, 1916 Race St., Philadelphia, PA 19103.

U.S. Environmental Protection Agency
CLP Sample Management Office
P. O. Box 818, Alexandria, Virginia 22313
PHONE: (703)/557-2490 or FTS/557-2490

SAS Number

SPECIAL ANALYTICAL SERVICES
Client Request

☒

Regional Transmittal

☐

Telephone Request

- A. EPA Region/Client: Region V WW Engineering & Science
- B. RSCC Representative: Jan Pels
- C. Telephone Number: 312/ 353-2720
- D. Date of Request: _____
- E. Site Name: Skinner Landfill - West Chester, Ohio

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. General description of analytical service requested: Analysis of high hazard waste samples for Proximate Analysis (moisture, volatile matter, fixed carbon) and Heating Value by ASTM methods.
2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium, or high concentration):
58 high hazard waste samples.
Includes duplicates and blanks.
3. Purpose of analysis (specify whether Superfund (Remedial or Enforcement), RCRA, NPDES, etc.):
Superfund - Remedial Action

4. Estimated date(s) of collection: _____
5. Estimated date(s) and method of shipment: Daily by overnight carrier.
6. Number of days analysis and data required after laboratory receipt of samples:
Laboratory should report results within 30 days.
7. Analytical protocol required (attach copy if other than a protocol currently used in this program):
Proximate Analysis by ASTM D3172. This includes moisture by ASTM D3173; volatile matter by ASTM D3175, and fixed carbon by difference (ASTM D3172 Section 6.4).
Analysis of Heating Value by ASTM D2015. (see attached)

3. Special technical instruction (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.): _____
Samples may be toxic/flammable.
Analysis must be performed in conjunction with the Ultimate Analysis SAS for this project.

9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.). If not completed, format of results will be left to program discretion.
Supply copies of raw data, bench sheets, calibration results, sample and QA/QC data for each procedure. All records must be legible and sufficient to recalculate sample values.

10. Other (use additional sheets or attach supplementary information, as needed):

11. Name of sampling/shipping contact: Bob Phillips
Phone: 616/ 942-9600 EXT 263

I. DATA REQUIREMENTS

<u>Parameter:</u>	<u>Detection Limit</u>	<u>Precision Desired</u> <u>(+/- % or Conc.)</u>
<u>Moisture</u>	<u>less than 1%</u>	<u>I 20%</u>
<u>Volatile Matter</u>	<u>less than 1%</u>	<u>I 20%</u>
<u>Fixed Carbon</u>	<u>less than 1%</u>	<u>by difference NA</u>
<u>Heating Value</u>	<u>50 BTU/lb</u>	<u>I 20%</u>
<u> </u>	<u> </u>	<u> </u>
<u> </u>	<u> </u>	<u> </u>

II. QC REQUIREMENTS

<u>Audits Required</u>	<u>Frequency of Audits</u>	<u>Limits* (% or Conc.)</u>
<u>Duplicates</u>	<u>1 per 10 samples</u>	<u>+ 20%</u>
<u>Blanks</u>	<u>1 per 10 samples</u>	<u>+ 20%</u>
<u>NBS Reference Material</u>	<u>1 per 10 samples</u>	<u>+ 20%</u>
<u> </u>	<u> </u>	<u> </u>
<u> </u>	<u> </u>	<u> </u>
<u> </u>	<u> </u>	<u> </u>
<u> </u>	<u> </u>	<u> </u>

III. ACTION REQUIRED IF LIMITS ARE EXCEEDED:

Rerun sample set if blanks, duplicates, or reference material exceeds QA/QC limits.

Contact: Jan Pels 312/ 353-2720 or Chuck Ellv 312/ 353-9007

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for special analytical services. Should you have any questions or need any assistance, please call the Sample Management Office.



Standard Method for Proximate Analysis of Coal and Coke¹

This standard is issued under the fixed designation D 3172; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (^ε) indicates an editorial change since the last revision or reapproval.

¹ NOTE—Section 4 was added editorially in September 1984.

1. Scope

1.1 This method covers the determination of moisture, volatile matter, and ash and the calculation of fixed carbon on coals and cokes sampled and prepared by prescribed methods and analyzed according to ASTM established procedures.

1.2 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of whoever uses this standard to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 ASTM Standards:

- D 346 Method of Collection and Preparation of Coke Samples for Laboratory Analysis²
- D 388 Classification of Coals by Rank²
- D 2013 Method of Preparing Coal Samples for Analysis²
- D 2234 Method for Collection of a Gross Sample of Coal²
- D 3173 Test Method for Moisture in the Analysis Sample of Coal and Coke²
- D 3174 Test Method for Ash in the Analysis Sample of Coal and Coke from Coal²
- D 3175 Test Method for Volatile Matter in the Analysis Sample of Coal and Coke²

¹ This method is under the jurisdiction of ASTM Committee D-5 on Coal and Coke and is the direct responsibility of Subcommittee D05.21 on Methods of Analysis.

Current edition approved April 27, 1973. Published July 1973.

² Annual Book of ASTM Standards, Vol 05.05.

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This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, 1916 Race St., Philadelphia, PA 19103.

3. Definition

3.1 *proximate analysis of coal and coke*—an assay of the moisture, ash, volatile matter, and fixed carbon as determined by prescribed methods. Other constituents such as sulfur and phosphorus are not included.

4. Significance and Use

4.1 Methods, as herein described, may be used to establish the rank of coals, to show the ratio of combustible to incombustible constituents, to provide the basis for buying and selling, and to evaluate for beneficiation or for other purposes.

5. Sampling

5.1 Coal sample collection shall be in accordance with Sections 5 and 6 of Classification D 388, if the proximate analysis is to be used for classification of coal by rank. In all other cases, sample collection shall be in accordance with Methods D 2234. Preparation shall be in accordance with Method D 2013. Coke sampling shall be in accordance with Method D 346.

6. Test Methods

6.1 *Moisture*—Test Method D 3173.

6.2 *Ash*—Test Method D 3174.

6.3 *Volatile Matter*—Test Method D 3175. If the modified procedure is required, the report should show that the modified procedure was used.

6.4 *Fixed Carbon*—The fixed carbon is a calculated value. It is the resultant of the summation of percentage moisture, ash, and volatile matter subtracted from 100. All percentages shall be on the same moisture reference base.

Fixed carbon, % = 100 - (moisture, %
+ ash, % + volatile matter. %)

1. Scope

1.1 This method covers the analysis of coals and cokes for moisture, volatile matter, ash, and fixed carbon. The analysis is performed in conjunction with the analysis of sulfur and phosphorus. The results are used for the determination of the rank of the coal, the ratio of combustible to incombustible constituents, the basis for buying and selling, and the evaluation for beneficiation or for other purposes.

2. Referenc

2.1 ASTM Standards:
D 346 Method of Collection and Preparation of Coke Samples for Laboratory Analysis²
D 2013 Method of Preparing Coal Samples for Analysis²
D 2234 Method for Collection of a Gross Sample of Coal²
D 3173 Test Method for Moisture in the Analysis Sample of Coal and Coke²
D 3174 Test Method for Ash in the Analysis Sample of Coal and Coke from Coal²
D 3175 Test Method for Volatile Matter in the Analysis Sample of Coal and Coke²

3. Summar

3.1 Moisture, ash, and volatile matter are determined by the methods described in this standard. The results are used for the determination of the rank of the coal, the ratio of combustible to incombustible constituents, the basis for buying and selling, and the evaluation for beneficiation or for other purposes.

4. Signific

4.1 Moisture, ash, and volatile matter are determined by the methods described in this standard. The results are used for the determination of the rank of the coal, the ratio of combustible to incombustible constituents, the basis for buying and selling, and the evaluation for beneficiation or for other purposes.

¹ This test method is under the jurisdiction of ASTM Committee D-5 on Coal and Coke and is the direct responsibility of Subcommittee D05.21 on Methods of Analysis.
Current edition approved April 27, 1973. Published July 1973.
² Annual Book of ASTM Standards, Vol 05.05.



Designation: D 3173 - 87^{e1}

Standard Test Method for Moisture in the Analysis Sample of Coal and Coke¹

This standard is issued under the fixed designation D 3173; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reappraisal. A superscript epsilon (^e) indicates an editorial change since the last revision or reappraisal.

¹ NOTE—Section 7.1 was corrected editorially in July 1988.

1. Scope

1.1 This test method covers the determination of moisture in the analysis sample of coal or coke. It is used for calculating other analytical results to a dry basis. When used in conjunction with the air drying loss as determined in accordance with Method D 2013 or Method D 346, each analytical result can be calculated to an as-received basis:

1.2 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. See Note.*

2. Referenced Documents

2.1 ASTM Standards:

- D 346 Method of Collection and Preparation of Coke Samples for Laboratory Analysis²
- D 2013 Method of Preparing Coal Samples for Analysis²
- D 3180 Method for Calculating Coal and Coke Analyses from As-Determined to Different Bases²
- D 3302 Test Method for Total Moisture in Coal²

3. Summary of Method

3.1 Moisture is determined by establishing the loss in weight of the sample when heated under rigidly controlled conditions of temperature, time and atmosphere, sample weight, and equipment specifications.

4. Significance and Use

4.1 Moisture as determined by this test method is used for calculating other analytical results to a moisture free basis using procedures in Method D 3180. Moisture percent determined by this test method may be used in conjunction with the air-dry moisture loss determined in Method D 2013 and Test Method D 3302 to determine total moisture in coal. Total moisture is used for calculating other analytical results to "as received" basis using Method D 3180. Moisture, ash, volatile, matter, and fixed carbon percents constitute the proximate analysis of coal and coke.

5. Analysis Sample

5.1 The analysis sample is that sample which has been pulverized to pass 250- μ m (No. 60) sieve. Weigh and record the percent passing through the sieve.

6. Apparatus

6.1 Drying Oven, for coal samples:

6.1.1 For determining the moisture of coal, the oven shall be so constructed as to have a uniform temperature in all parts, have a minimum of air space, and be capable of temperature regulation between the limits of 104 and 110°C. It may be of the form shown in Fig. 1. Provision shall be made for renewing the reheated air in the oven at the rate two to four times a minute, with the air dried as defined in 7.1.

6.1.2 In the oven shown in Fig. 1, the door should contain a hole of approximately $\frac{1}{8}$ in. (3.2 mm) in diameter near the bottom to permit a free flow of air through the oven space.

6.2 *Drying Oven, for coke samples.* For determining the moisture of coke, an ordinary drying oven with openings for natural air circulation and capable of temperature regulation between limits of 104 and 110°C may be used.

6.3 *Capsules, with covers.* A convenient form, which allows the ash determination to be made on the same sample, is a porcelain capsule, $\frac{3}{8}$ in. (22 mm) in depth and $1\frac{1}{4}$ in. (44 mm) in diameter, or a fused silica capsule of similar shape. These capsules shall be used with a well-fitting flat aluminum cover, illustrated in Fig. 2. Platinum crucibles or glass capsules with ground-glass caps may also be used. They should be as shallow as possible, consistent with convenient handling.

7. Reagents

7.1 *Dry Air*—Air used to purge the drying oven should be dried to a moisture content of 1.9 mg/L or less. (Dew point -10°C or less.) Any desiccant or drying method capable of achieving this degree of dryness is suitable.

7.2 *Desiccants*—Materials suitable for use in the desiccator may be chosen from the following:

7.2.1 *Anhydrous Calcium Sulfate* (0.004 mg/L).

7.2.2 *Silica Gel.*

7.2.3 *Magnesium Perchlorate* (0.0005 mg/L).

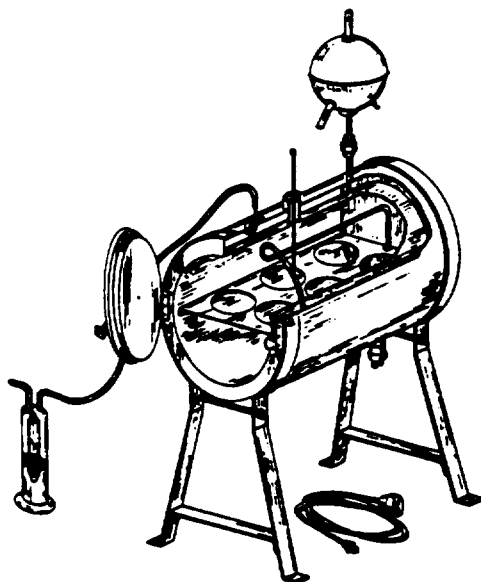
7.2.4 *Sulfuric Acid, Concentrated* (0.003 mg/L).

7.2.5 The desiccant must be kept fresh enough to assure that the air in the desiccator is dry as defined in 7.1. Values in parentheses () are literature values for the residual

¹ This test method is under the jurisdiction of ASTM Committee D-5 on Coal and Coke and is the direct responsibility of Subcommittee D05.21 on Methods of Analysis.

Current edition approved June 8, 1987. Published August 1987. Originally published as D 3173 - 73. Last previous edition D 3173 - 85.

² Annual Book of ASTM Standards, Vol 05.05.



NOTE—Details in U.S. Bureau of Mines Bulletin No. 482, 1951, p 6
FIG. 1 Moisture Oven

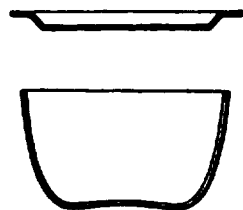


FIG. 2 Capsule for Use in Determining Moisture

amount of moisture in air at equilibrium with these desiccants.

NOTE—Warning: Sulfuric acid is corrosive and can cause severe damage to eyes, skin, and clothing. Magnesium perchlorate is a strong oxidant and can react violently with organic materials.

8. Procedure for Sample Passing a 250- μ m (No. 60) Sieve

8.1 Heat the empty capsules under the conditions at

which the sample is to be dried, place the stopper or cover on the capsule, cool over a desiccant for 15 to 30 min, and weigh. Dip out with a spoon or spatula from the sample bottle approximately 1 g of the sample. Put this quickly into the capsule, close, and weigh at once to the nearest ± 0.1 mg.

8.2 An alternative procedure for weighing the sample (more subject to error) is as follows: After transferring an amount of the sample slightly in excess of 1 g, bring to exactly 1 g in weight (± 0.5 mg) by quickly removing the excess weight of the sample with a spatula. The utmost dispatch must be used in order to minimize the exposure of the sample until the weight is determined.

8.3 After removing the covers, quickly place the capsules in a preheated oven (at 104 to 110°C) through which passes a current of dry air. (The current of dry air is not necessary for coke.) Close the oven at once and heat for 1 h. Open the oven, cover the capsules quickly, cool in a desiccator over desiccant, and weigh as soon as the capsules have reached room temperature.

8.4 Use the percentage of moisture in the sample passing a 250- μ m (No. 60) sieve to calculate the results of the other analyses to a dry basis.

9. Calculations

9.1 Calculate the percent moisture in the analysis sample as follows:

$$\text{Moisture in analysis sample, \%} = [(A - B)/A] \times 100$$

where:

A = grams of sample used, and
 B = grams of sample after heating.

10. Precision and Bias

10.1 The following criteria should be used for judging the acceptability of results:

10.1.1 *Repeatability*—Duplicate results by the same laboratory should not be considered suspect unless they differ by more than 0.2 % for coals having less than 5 % moisture and 0.3 % for coals having more than 5 % moisture.

10.1.2 *Reproducibility*—The results submitted by two or more laboratories should not be considered suspect unless they differ by more than 0.3 % for coals having less than 5 % moisture and 0.5 % for coals having more than 5 % moisture.

10.1.3 *Bias*—Certified standards are not available for the determination of bias by this test method.

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This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, 1916 Race St., Philadelphia, PA 19103.

1. Scope

1.1 This method is for the determination of moisture in organic residues prepared in accordance with D 346. The proximate analysis, constitute: D 2795 ash.

2. Reference

2.1 AS
D 121
D 346
Sam
D 388
D 1756
D 1757
Coke
D 2013
D 2795
D 3172
D 3173
of C
D 3176
D 3180
from
D 3682
Coal

3. Summary

3.1 Ash after burning condition and equip

4. Significance

4.1 Ash remaining differs in present in of all water conversion

¹ This method is for the determination of moisture in organic residues prepared in accordance with D 346. The proximate analysis, constitute: D 2795 ash.
Current edition published as
² Annual Book of ASTM Standards



Standard Test Method for Volatile Matter in the Analysis Sample of Coal and Coke¹

This standard is issued under the fixed designation D 3175; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This method determines the percentage of gaseous products, exclusive of moisture vapor, in the analysis sample which are released under the specific conditions of the test.

2. Referenced Document

2.1 *ASTM Standard:*
D3173 Test Method for Moisture in the Analysis Sample of Coal and Coke²

3. Summary of Method

3.1 Volatile matter is determined by establishing the loss in weight resulting from heating a coal or coke under rigidly controlled conditions. The measured weight loss, corrected for moisture as determined in Test Method D 3173 establishes the volatile matter content. Two procedures are described to permit conformity with differences in sample behavior.

4. Significance and Use

4.1 Volatile matter, when determined as herein described, may be used to establish the rank of coals, to indicate coke yield on carbonization process, to provide the basis for purchasing and selling, or to establish burning characteristics.

5. Definition

5.1 *sparking fuels*—within the context of this standard, fuels that do not yield a coherent cake as residue in the volatile matter determination but do evolve gaseous products at a rate sufficient to mechanically carry solid particles out of the crucible when heated at the standard rate. Such coals normally include all low-rank noncaking coals and lignites but may also include those anthracites, semianthracites, bituminous, chars and cokes that lose solid particles as described above. These are defined as "sparking fuels" because particles escaping at the higher temperatures may become incandescent and spark as they are emitted.

6. Apparatus

6.1 *Platinum Crucible*, with closely fitting cover, for coal. The crucible shall be of not less than 10 or more than 20-mL

capacity, not less than 25 or more than 35 mm in diameter, and not less than 30 or more than 35 mm in height.

6.2 *Platinum Crucible*, with closely fitting cover, for coke. The crucible shall be of 10-mL capacity, with capsule cover having thin flexible sides fitting down into crucible. Or the double-crucible method may be used, in which the sample is placed in 10-mL platinum crucible, which is then covered with another crucible of such a size that it will fit closely to the sides of the outer crucible and its bottom will rest $\frac{1}{3}$ to $\frac{1}{2}$ in. (8.5 to 12.7 mm) above the bottom of the outer crucible.

6.3 *Vertical Electric Tube Furnace*, for coal or coke. The furnace may be of the form shown in Fig. 1. It shall be regulated to maintain a temperature of $950 \pm 20^\circ\text{C}$ in the crucible, as measured by thermocouple positioned in the furnace.

7. Procedure

7.1 Procedure for Nonsparking Coals and Cokes:

7.1.1 Weigh 1 g of the sample in a weighed platinum crucible, close with a cover (Note 1), place on platinum or Nichrome-wire supports and insert directly into the furnace chamber, which shall be maintained at a temperature of $950 \pm 20^\circ\text{C}$, and lower immediately to the 950 zone. Regulation of the temperature to within the prescribed limits is critical. After the more rapid discharge of volatile matter has subsided as shown by the disappearance of the luminous flame or, in the case of coke after 2 or 3 min, inspect the crucible (Note 2) to verify the lid is still properly seated. If necessary, reseal the lid to guard against the admission of air into the crucible. Do this as rapidly as possible by raising the crucible to the top of the furnace chamber, reposition the lid (Note 3) to more perfectly seal the crucible, then lower immediately back to the 950 zone. After heating for a total of exactly 7 min, remove the crucible from the furnace and, without disturbing the cover, allow it to cool. Coke should be cooled in a desiccator. Weigh as soon as cold. The percentage loss of weight minus the percentage moisture equals the volatile matter.

NOTE 1—The cover should fit closely enough so that the carbon deposit from bituminous, subbituminous, and lignite coals does not burn away from the under side.

NOTE 2—Inspection of the crucible may be aided by the use of a mirror held above the furnace well.

NOTE 3—With some strongly caking low-volatile and medium-volatile bituminous coals, the coke button may be broken with explosive violence, due to the liberation of volatile matter within the button. This is usually designated as "popping." Such popping may blow the lid off the crucible and cause mechanical losses of the coked material. When such popping is observed, the determination shall be rejected and the test repeated until popping does not occur.

¹ This method is under the jurisdiction of ASTM Committee D-5 on Coal and Coke and is the direct responsibility of Subcommittee D05.21 on Methods of Analysis.

Current edition approved Aug. 27, 1982. Published December 1982. Originally published as D 3175 - 73. Last previous edition D 3175 - 77.

² Annual Book of ASTM Standards, Vol 05.05.

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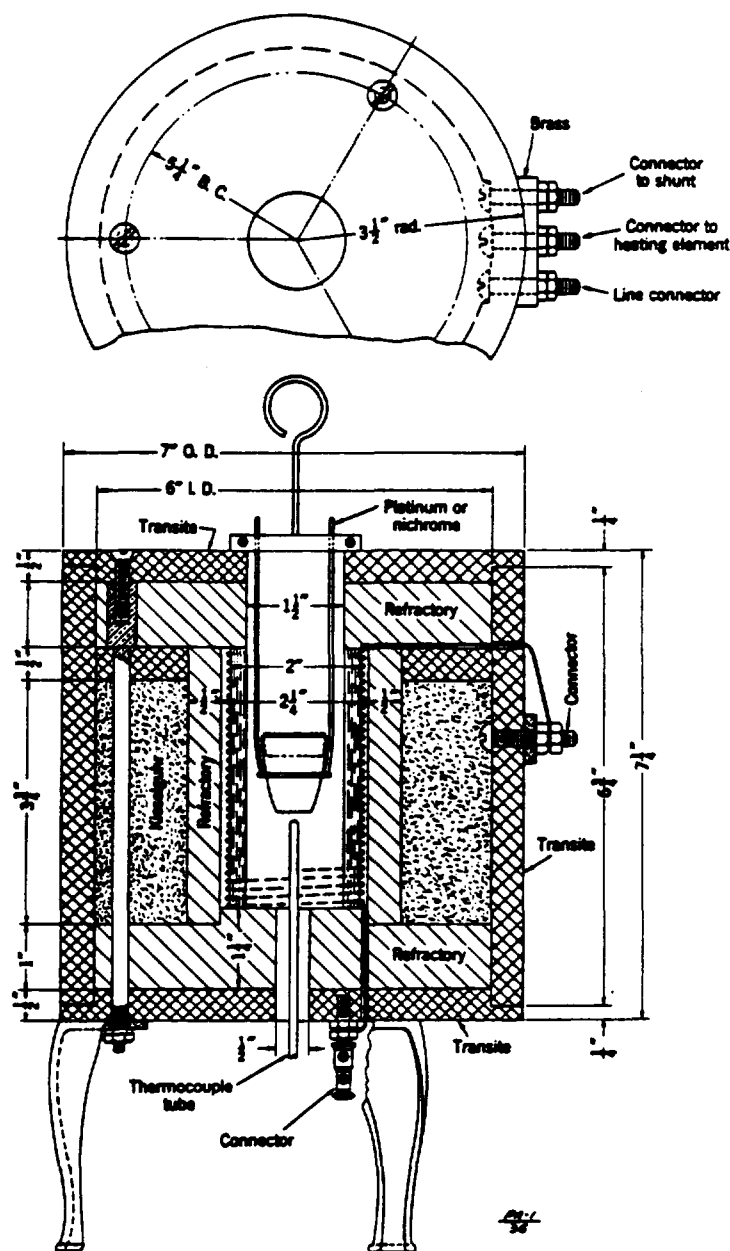


FIG. 1 Electric Furnace for Determining Volatile Matter

7.2 Modified Procedure for All Sparking Fuels:

7.2.1 Fuels that do not cake or cake weakly when volatile matter is determined shall be watched closely for sparking during the heating period (Note 2); also, at the end of the test the crucible cover shall be inspected for ash deposits, and the presence of such deposits shall be considered as evidence of sparking.

7.2.2 All fuels that spark when the volatile is determined by the methods described in 7.1 shall be treated as follows: The sample shall be given a preliminary gradual heating such that a temperature of $600 \pm 50^\circ\text{C}$ is reached in 6 min (Note

4). After this preliminary heating the sample shall be heated for exactly 6 min at $950 \pm 20^\circ\text{C}$. If sparking is then observed, the determination shall be rejected and the test repeated until no sparking occurs either during the preliminary heating or during the 6-min period at 950°C . Remove the crucible from the furnace, cool on a metal cooling block (Note 5) and weigh. The percentage loss in weight minus the percent moisture in accordance with Test Method D 3173, is the volatile matter. All analyses by this method shall be so marked when reported to indicate that the modified procedure was used.

NOTE 4—If a tubular furnace of the Fieldner type (Fig. 1) is used for the determination of volatile matter, the preliminary gradual heating may be accomplished by moving the crucible to predetermined positions in the cooler top zone of the furnace. Due to variations in the heating characteristics of the furnace, the operator must predetermine by thermocouple the proper positions to meet a preliminary heating rate as specified in 7.2.2. A mechanical device to lower the crucible into the furnace may be used to facilitate control of the lowering operation.

NOTE 5—To ensure uniformity of results, the cooling period should be kept constant and should not be prolonged beyond 15 min.

8. Calculations

8.1 Calculate the weight loss percent as follows:

$$\text{Weight loss, \%} = (A - B)/A \times 100$$

where:

A = weight of sample used, g, and

B = weight of sample after heating, g.

8.2 Calculate the volatile matter percent in the analysis samples as follows:

$$\text{Volatile matter in analysis sample, \%} = C - D$$

where:

C = weight loss, %, and

D = moisture, %.

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9. Precision

9.1 The following criteria should be used for judging the acceptability of results:

9.1.1 *Repeatability*—Duplicate results by the same laboratory should not be considered suspect unless they differ by more than the following percentages:

High-temperature coke	0.2
Anthracite	0.3
Semianthracite, bituminous coal, low-temperature coke, and chars	0.5
Subbituminous	0.7
Lignite and peat	1.0

9.2.1 *Reproducibility*—The results submitted by two or more laboratories should not be considered suspect unless they differ by more than the following percentages:

High-temperature coke	0.4
Anthracite	0.6
Semianthracite, bituminous coal, low-temperature coke, and chars	1.0
Subbituminous	1.4
Lignite and peat	2.0

1. Scope

1.1 This standard is applied to derived is industries or for oth

1.2 This standard addresses the responsibility to establish mine the

2. Reference

2.1 ASTM D 346

Sample 13

2234

D 2361

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D 3172

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Sample

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3. Significance

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Standard Test Method for GROSS CALORIFIC VALUE OF COAL AND COKE BY THE ADIABATIC BOMB CALORIMETER¹

This standard is issued under the fixed designation D 2015; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the determination of the gross calorific value of coal and coke by the adiabatic bomb calorimeter.

1.2 The values stated in SI units are to be regarded as the standard.

1.3 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of whoever uses this standard to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. Specific precautionary statements are given in Section 9.*

2. Applicable Documents

2.1 ASTM Standards:

D 121 Definitions of Terms Relating to Coal and Coke²

D 346 Method of Collection and Preparation of Coke Samples for Laboratory Analysis²

D 1193 Specification for Reagent Water³

D 2013 Method of Preparing Coal Samples for Analysis²

D 3173 Test Method for Moisture in the Analysis Sample of Coal and Coke²

D 3177 Test Methods for Total Sulfur in the Analysis Sample of Coal and Coke²

D 3180 Method for Calculating Coal and Coke Analyses from As-Determined to Different Bases²

D 4239 Test Method for Sulfur in the Analysis Sample of Coal and Coke Using High Temperature Tube Furnace Combustion Methods²

E 1 Specification for ASTM Thermometers⁴

E 144 Recommended Practice for Safe Use of Oxygen Combustion Bombs⁵

3. Terminology

3.1 Definitions:

3.1.1 *calorific value*—the heat produced by combustion of a unit quantity of a substance under specified conditions. It is expressed in this test method in British thermal units per pound (Btu/lb). Calorific value may also be expressed in calories per gram (cal/g) or in the International System of Units (SI), joules per gram (J/g), when required. The unit equivalents are given in Table 1.

3.1.2 *gross calorific value (gross heat of combustion at constant volume) Q_g (gross)*—see Definitions D 121.

3.1.3 *net calorific value (net heat of combustion at constant pressure) Q_p (net)*—see Definitions D 121.

3.1.4 *calorimeter*—as used in this test method, consists of the bomb and its contents, the calorimeter vessel (bucket) with stirrer, the water in which the bomb is immersed, and the portions of the thermometer and the ignition leads within the calorimeter vessel.

3.2 Description of Terms Specific to This Standard:

3.2.1 *corrected temperature rise*—the temperature change of the calorimeter caused by the process that occurs inside the bomb, that is, the observed temperature change corrected for various effects as noted in 10.4.1.

NOTE 1—Temperature is measured in either degrees

¹ This test method is under the jurisdiction of ASTM Committee D-5 on Coal and Coke and is the direct responsibility of Subcommittee D05.21 on Methods of Analysis.

Current edition approved Aug. 23, 1985. Published October 1985. Originally published as D 2015 - 62 T. Last previous edition D 2015 - 77 (1978).

² Annual Book of ASTM Standards, Vol 05.05.

³ Annual Book of ASTM Standards, Vol 11.01.

⁴ Annual Book of ASTM Standards, Vol 14.01.

⁵ Annual Book of ASTM Standards, Vol 14.02.

Celsius or degrees Fahrenheit. Thermometer corrections should be applied. Temperatures may be recorded in ohms or other arbitrary units instead of degrees. Consistent units must be used in standardization and the actual calorific value determination. If arbitrary units other than degrees Celsius or Fahrenheit are used, the temperature interval over which all tests are made, must not vary so much that an error greater than 0.001°C would be caused.

3.2.2 energy equivalent, heat capacity, or water equivalent—the energy required to raise the temperature of the calorimeter one arbitrary unit. This is the quantity that, when multiplied by the corrected temperature rise, then adjusted for extraneous heat effects, and divided by the mass of the sample, gives the gross calorific value.

NOTE 2—Energy units for quantities listed throughout this test method are such that the number of energy units per gram of sample corresponds exactly to the number of Btu's per pound of sample. For brevity these are referred to as Btu's. The actual energies are smaller than those stated by the ratio of the number of pounds per gram (1/453.59). The energy equivalent of the calorimeter has the units (Btu/lb) times (g/degree). Conversion to other units is discussed in Appendix X1.2. Time is expressed in minutes. Mass is expressed in grams.

4. Summary of Method

4.1 Calorific value is determined in this test method by burning a weighed sample, in oxygen, in a calibrated adiabatic bomb calorimeter under controlled conditions. The calorimeter is standardized by burning benzoic acid. The calorific value of the sample is computed from temperature observations made before, during and after combustion, making proper allowances for heat contributed by other processes, and for thermometer and thermochemical corrections.

NOTE 3—Oxidation after sampling of susceptible low-rank coal or lignite may result in a reduction of calorific value. Unnecessary exposure of the sample to air from the time of sampling or delay in analysis shall be avoided.

5. Significance and Use

5.1 The gross calorific value is used to compute the total calorific content of the quantity of coal represented by the sample for payment purposes, provided the buyer and the seller mutually agree upon this.

5.2 The gross calorific value is used in computing the calorific value versus sulfur content to determine if the coal meets regulatory requirements for industrial fuels.

5.3 The gross calorific value may be used for evaluating the effectiveness of beneficiation processes, or for research purposes.

esses, or for research purposes.

6. Apparatus and Facilities

6.1 Test Space, shall be a room or area free from drafts and that can be kept at a reasonably uniform temperature for the time required for the determination. The apparatus should be shielded from direct sunlight and radiation from other heat sources. Thermostatic control of room temperature and controlled relative humidity are desirable.

6.2 Combustion Bomb, shall be constructed of materials that are not affected by the combustion process or products sufficiently to introduce measureable heat input or alteration of end products. The bomb must be designed so that all liquid combustion products can be completely recovered by washing the inner surfaces. There must be no gas leakage during a test. The bomb must be capable of withstanding a hydrostatic pressure test of 20 MPa (3000 psig) at room temperature without stressing any part beyond its elastic limit.

6.3 Balance, shall be a laboratory balance having capability to weigh the sample to the nearest 0.0001 g. The balance should be checked periodically to determine its accuracy.

6.4 Calorimeter Vessel, shall be made of metal with a tarnish-resistant coating, and with all outer surfaces highly polished. Its size shall be such that the bomb will be completely immersed in water when the calorimeter is assembled. It shall have a device for stirring the water thoroughly and at a uniform rate, but with minimum heat input. Continuous stirring for 10 min shall not raise the calorimeter temperature more than 0.01°C (0.02°F) starting with identical temperatures in the calorimeter, room, and jacket. The immersed portion of the stirrer shall be coupled to the outside through a material of low-heat conductivity.

6.5 Jacket, shall be a double-walled, water-filled jacket fully enclosing the calorimeter. The sides, top, and bottom of the calorimeter vessel shall be approximately 10 mm from the inner wall of the jacket to minimize convection currents. Mechanical supports for the calorimeter vessel shall provide as little thermal conduction as possible. The jacket shall have a device for stirring the water thoroughly and at a uniform rate with minimum heat input.

6.6 Thermometers, used to measure temperature in the calorimeter and jacket shall be any of



the following types or combinations thereof:

6.6.1 *Liquid-in-Glass Thermometers*, conforming to the requirements for ASTM Thermometers 56C, 56F, 116C, or 117C as prescribed in Specification E 1. The thermometers shall be tested for accuracy against a known standard (preferably by the National Bureau of Standards). For Thermometers 56C and 56F the calibration should be at intervals no larger than 2.0°C or 2.5°F over the entire graduated scale. The maximum difference in correction between any two test points shall be no more than 0.02°C or 0.05°F. For Thermometers 116C and 117C, the calibration should be at intervals no larger than 0.5°C over the entire calibrated range. The maximum difference in correction between any two test points shall not be more than 0.02°C.

6.6.2 *Beckman Differential Thermometer*, (glass enclosed scale, adjustable), having a range of approximately 6°C in 0.01°C subdivisions reading upward and conforming to the requirements for Thermometer 115C, as prescribed in Specification E 1, may be used. Each of these thermometers shall be tested for accuracy against a known standard (preferably by the National Bureau of Standards) at intervals no larger than 1°C over the entire graduated scale. The maximum difference in the correction between any two test points shall not be more than 0.02°C.

6.6.3 *Other Thermometers*, of an accuracy equal to or better than 0.001°C, such as platinum resistance or linear thermistor thermometers, are satisfactory and may be used if properly calibrated. A Wheatstone bridge and galvanometer capable of measuring resistance to 0.0001 Ω are necessary for use with 25 Ω platinum resistance thermometers.

6.7 *Thermometer Accessories*—A magnifier is required for reading liquid-in-glass thermometers to one-tenth of the smallest scale division. This shall have a lens and holder designed so as to introduce no significant errors due to parallax.

6.8 *Sample Holder*, shall be an open crucible of platinum, quartz, or acceptable base-metal alloy. Base-metal alloy crucibles are acceptable, if after a few preliminary firings, the weight does not change significantly between tests.

6.9 *Ignition Wire*, shall be 100 mm of 0.16 mm diameter (No. 34 B & S gage) nickel-chromium (Chromel C) alloy or iron wire. Platinum or palladium wire, 0.10 mm diameter (No. 38 B & S gage), may be used, provided constant ignition energy is supplied. The length, or mass, of

the ignition wire shall remain constant for all calibrations and calorific value determinations.

6.10 *Ignition Circuit*, for ignition purposes shall provide 6 to 16 V alternating or direct current to the ignition wire. An ammeter or pilot light is required in the circuit to indicate when current is flowing. A step-down transformer, connected to an alternating current lighting circuit or batteries, may be used.

6.11 *Buret*, used for the acid titration shall have 0.1-mL divisions.

6.12 *Automated Controller and Temperature Measuring Accessories*, may be used.

7. Reagents

7.1 *Reagent Water*, conforming to Type II of Specification D 1193, shall be used for preparation of reagents and washing of the bomb interior.

7.2 *Purity of Reagents*, reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.⁶ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.3 *Benzoic Acid*, (C₆H₅COOH), shall be the National Bureau of Standards benzoic acid. The crystals shall be pelleted before use. Commercially prepared pellets may be used provided they are made from National Bureau of Standards benzoic acid. The value of heat of combustion of benzoic acid for use in the calibration calculations shall be in accordance with the value listed in the National Bureau of Standards certificate issued with the standard.

7.4 *Methyl Orange, Methyl Red, or Methyl Purple Indicator*, may be used to titrate the acid formed during combustion. The indicator used shall be the same for both calibration and calorific value determinations.

7.5 *Oxygen*, shall be free of combustible matter. Only oxygen manufactured from liquid air, guaranteed to be greater than 99.5 % pure,

⁶ "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, NY, and the "United States Pharmacopeia."

should be used. Oxygen made by the electrolytic process may contain a small amount of hydrogen rendering it unfit without purification.

7.6 *Sodium Carbonate Standard Solution*, (Na_2CO_3), should be dried for 24 h at 105°C. Dissolve 20.9 g in water and dilute to 1 L. One millilitre of this solution is equivalent to 10.0 Btu in the nitric acid (HNO_3) titration.

8. Sample

8.1 The sample shall be the material pulverized to pass No. 60 (250- μm) sieve, prepared in accordance with either Method D 346 for coke, or Method D 2013 for coal.

8.2 A separate portion of the analysis sample should be analyzed simultaneously for moisture content in accordance with Method D 2013 and Test Method D 3173, so that calculation to other bases can be made.

8.3 Sulfur analysis shall be made in accordance with Test Methods D 3177.

9. Safety Precautions

9.1 The following precautions are recommended for safe calorimeter operation. Additional precautions are given in Recommended Practice E 144. Also consult the calorimeter manufacturer's installation and operating manuals before using the calorimeter.

9.2 The mass of coal or coke sample and the pressure of the oxygen admitted to the bomb must not exceed the manufacturer's recommendations.

9.3 Bomb parts should be inspected carefully after each use. Threads of the main closure should be checked frequently for wear. Cracked or significantly worn parts should be replaced. The bomb should be returned to the manufacturer occasionally for inspection and possible proof firing.

9.4 The oxygen supply cylinder should be equipped with an approved type of safety device, such as a reducing valve, in addition to the needle valve and pressure gage used in regulating the oxygen feed to the bomb. Valves, gages, and gaskets must meet industry safety code. Suitable reducing valves and adaptors for 3 to 4-MPa (300 to 500-psi) discharge pressure are obtainable from commercial sources of compressed gas equipment. The pressure gage shall be checked periodically for accuracy.

9.5 During ignition of a sample, the operator

must not permit any portion of her/his body to extend over the calorimeter.

9.6 When combustion aids are employed, extreme caution must be exercised not to exceed the bomb manufacturer's recommendations and to avoid damage to the bomb. Do not fire loose fluffy material such as unpelleted benzoic acid, unless thoroughly mixed with the coal sample.

9.7 Do not fire the bomb if the bomb has been dropped or turned over after loading, or if there is evidence of a gas leak when the bomb is submerged in the calorimeter water.

9.8 For manually operated calorimeters, the ignition circuit switch shall be of the momentary double-contact type, normally open, except when held closed by the operator. The switch should be depressed only long enough to fire the charge.

10. Standardization

10.1 The calorimeter is standardized by combustion of benzoic acid.

10.2 Determine the energy equivalent of the calorimeter for a specific temperature rise as the average of a series of ten individual runs made over a period of not less than 3 days nor more than 5 days. To be acceptable, the standard deviation of the series shall be 6.5 Btu/°C (3.6 Btu/°F) or less (see Table 2). For this purpose, any individual test may be discarded only if there is evidence indicating incomplete combustion. If this limitation is not met, investigate for the source of the problem, correct it, then repeat the entire series to obtain a standard deviation within the acceptable limit.

10.3 Procedure:

10.3.1 Regulate the weights of the pellets of benzoic acid in each series to yield approximately the same temperature rise as that obtained with the coal tested in the same laboratory. The usual range of masses is 0.9 to 1.3/g. Weigh the pellet to the nearest 0.0001 g in the sample holder in which it is to be burned, and record the weight as the mass.

10.3.2 Rinse the bomb, invert to drain, and leave undried. Add 1.0 mL of water to the bomb prior to assembly for a determination.

10.3.3 Connect a measured length of ignition wire to the ignition terminals, with enough slack to allow the ignition wire to maintain contact with the sample.

10.3.4 Assemble the bomb and charge it with oxygen to a consistent pressure between 2 to 3

MPa (20 and 30 atm). This pressure must remain the same for each calibration and each calorific-value determination. Admit the oxygen slowly into the bomb so as not to blow powdered material from the sample holder. If the pressure exceeds the specified pressure, do not proceed with the combustion. Instead, detach the filling connection, exhaust the bomb in the usual manner, and discard the sample.

10.3.5 Fill the calorimeter vessel (bucket) with the measured (or weighed) quantity of water adjusted from 1.0 to 2.0°C (2.0 to 4.0°F) below room temperature, but not lower than 20°C (68°F). Use the same mass of water in each test weighed to +0.5 g. For 2000-mL calorimeters, the proper quantity can be obtained by use of a volumetric flask calibrated to deliver 2000 ± 0.5 mL. As the density of water varies with temperature, make suitable corrections if the water temperature varies from the temperature at which the flask was calibrated. Place the assembled bomb in the calorimeter vessel. Check that no oxygen bubbles are leaking from the bomb. Place the calorimeter vessel in the jacket; connect the electrodes; place the stirrers, thermometers, and cover in position. Start the stirrers and continue to operate them throughout the determination. Examine the thermometers for liquid separation and correct any separation before proceeding. The starting temperature should be within ±0.5°C (0.9°F) of that used in analysis of coal or coke samples.

NOTE 4—Check all liquid-in-glass thermometers at least daily for defects, for example, cracked glass, etc.

10.3.6 Allow 5 min for attainment of equilibrium. Adjust the jacket temperature to match the calorimeter temperature within 0.01°C (0.02°F) and maintain for 3 min. Use a magnifier when using ASTM Bomb Calorimeter Thermometers 56C or 56F, and estimate all readings (except those during the rapid-rise period) to the nearest 0.002°C or 0.005°F. Estimate ASTM Thermometers 115C, 116C, or 117C readings to 0.001°C, and 25 Ω resistance thermometer readings to the nearest 0.0001 Ω. Tap mercury thermometers (for instance, with a pencil) just before reading to avoid errors caused by mercury sticking to the walls of the capillary. Record the "initial temperature", t_i , 20°C (68°F) or higher, to within one-tenth of the smallest thermometer subdivision and ignite the charge. Adjust the jacket temperature to match that of the calorimeter tempera-

ture during the period of rise; keep the two temperatures as nearly equal as possible during the rapid rise and adjust to within 0.01°C (0.02°F) when approaching the final equilibrium temperature. Take calorimeter temperature readings at 1-min intervals until the same temperature, within one-tenth of the smallest thermometer subdivision, is observed in three successive readings. Record this as the "final temperature", t_f .

10.3.7 Open the cover and remove the bomb. Release the pressure at a uniform rate, such that the operation will require not less than 1 min. Open the bomb and examine the bomb interior. Discard the test if unburned sample or sooty deposits are found. Wash the interior of the bomb with distilled water containing the titration indicator, until the washings are free of acid, and titrate the washings with standard sodium carbonate solution.

10.3.8 Remove and measure, or weigh, the combined pieces of unburned ignition (firing) wire and subtract from the original length, or weigh to determine the wire consumed in firing. If the wire is weighed, remove the ball of oxidized metal from the end of each piece of wire before weighing.

10.4 Calculations:

10.4.1 *Temperature Rise*—Using data obtained as prescribed in 10.3.6, compute the corrected temperature rise, t , as follows:

$$t = t_f - t_i + C_s + C_r \quad (1)$$

where:

- t = corrected temperature rise, °C or °F,
- t_i = initial temperature reading at time of firing,
- t_f = final temperature reading,
- C_s = thermometer emergent stem correction, if required (see Note 5 and Annex A1.1.4, and
- C_r = thermometer setting correction, if required (see Note 5 and Annex A1.1.3)

NOTE 5—With all mercury-in-glass thermometers, it is necessary to make corrections if the total calorific value is altered by 5.0 Btu or more. This represents a change of 0.001°C or 0.002°F in a calorimeter using approximately 2000 g of water. Beckmann thermometers also require a setting correction and an emergent stem correction (Annex A1.1.3 and A1.1.4). Solid-stem ASTM Thermometers 56C and 56F do not require emergent stem corrections if all tests, including standardization, are performed within the same 5.5°C (10°F) interval. If operating temperatures range beyond this limit, a differential emergent stem correction (Annex A1.1.4) must be applied to the corrected tempera-

ture rise, t , in all tests including standardization.

10.4.2 *Thermochemical Corrections* (see Appendix X1.1, X1.2, and X1.3)—Compute the following for each test:

- e_1 = correction for the heat of formation of HNO_3 , in Btu. Each millilitre of standard Na_2CO_3 is equivalent to 10.0 Btu, and
- e_2 = correction for heat of combustion of firing wire, in Btu (Note 6).
0.41 Btu/mm or 2.6 Btu/mg for No. 34 B & S gage Chromel C.
0.49 Btu/mm or 3.2 Btu/mg for No. 34 B & S gage iron wire.

NOTE 6—There is no correction for platinum wire provided the ignition energy is constant.

10.4.3 Compute the calorimeter energy equivalent, E , by substituting in the following:

$$E = [(Hg) + e_1 + e_2]/t \quad (2)$$

where:

- E = calorimeter energy equivalent (Note 8),
- H = heat of combustion of benzoic acid, as stated in the National Bureau of Standards Certificate, Btu/lb in air,
- g = mass (weight in air) of benzoic acid, g,
- e_1 = titration correction (10.4.2),
- e_2 = fuse wire correction (10.4.2), and
- t = corrected temperature rise.

NOTE 7—Using the units and corrections as given in 10.4.1 and 10.4.2, the energy equivalent of the calorimeter is such that the calorific value of the coal sample will be obtained directly in British thermal units per pound when the mass of sample is taken in grams. The units of the energy equivalent are therefore: (Btu/lb) times (g/deg).

10.5 Repeat the procedure for a total of ten determinations. Compute the standard deviation as illustrated in Table 2.

11. Restandardization

11.1 Make checks on the energy equivalent value after changing the oxygen supply, after changing any part of the calorimeter, and at least once a month otherwise.

11.1.1 If a single new determination differs from the old value by 6 Btu/°C (4 Btu/°F), the old standard is suspect, thereby requiring a second test.

11.1.2 The difference between the two new determinations must not exceed 8 Btu/°C (5 Btu/°F), and the average of the two new determinations must not differ from the old standard by more than 4 Btu/°C (3 Btu/°F). If these require-

ments are met, do not change the calorimeter standard.

11.1.3 If the requirements given in 11.1.2 are not met, two more determinations must be run. The range of the four values must not exceed 14 Btu/°C (8 Btu/°F), and the average of the four new determinations must not differ from the old standard value by more than 3 Btu/°C (2 Btu/°F). If these requirements are met, do not change the calorimeter standard.

11.1.4 If the requirements given in 11.1.3 are not met, a fifth and sixth determination must be run. The range of the six new values must not exceed 17 Btu/°C (10 Btu/°F), and the average of the six new values must not differ from the old standard value by more than 2 Btu/°C (2 Btu/°F). If these requirements are met, do not change the calorimeter standard.

11.1.5 If the requirements given in 11.1.4 are not met, four more determinations must be run to complete a series of ten runs. The range of these ten results must not exceed 20 Btu/°C (12 Btu/°F), and the average of the ten new standards must not differ from the old standard by more than 1 Btu/°C (1 Btu/°F). If these requirements are met, do not change the calorimeter standard.

11.1.6 If the requirements given in 11.1.5 are not met, the average value from the ten new values must be used for the new standard energy equivalent, provided that the standard deviation of the series does not exceed 6.5 Btu/°C (3.6 Btu/°F).

11.2 The summary of the numerical requirements at each stage of restandardization is given in Table 3.

12. Procedure for Coal and Coke Samples (Note 8)

12.1 Thoroughly mix the analysis sample of coal or coke in the sample bottle and carefully weigh approximately 1 g of it into the sample holder. The sample shall be weighed to the nearest 0.0001 g. Make each determination in accordance with the procedure described in 10.3.2 through 10.3.8.

NOTE 8—For anthracite, coke, and coal of high ash content, that do not readily burn completely, one of the following procedures are recommended: (1) The inside of the sample holder is lined completely with ignited asbestos in a thin layer pressed well down in the angles, and the sample is then sprinkled evenly over the surface of the asbestos. (2) The mass of the sample may be varied to obtain good ignition. If the mass is varied, it will be necessary to recalibrate the calorimeter



so that the water equivalent will be based on the same temperature rise as that obtained with the sample weight. (3) A known amount of benzoic acid may be mixed with the sample. Proper allowance must be made for the heat of combustion of benzoic acid when determining the calorific value of the sample.

NOTE 9—For the calorific value of coke, it is necessary to use 3-MPa (30-atm) pressure for both standardization and analysis.

12.2 Determine the sulfur content of the sample by any of the procedures described in Test Methods D 3177.

13. Calculations (Note 2)

13.1 Compute the corrected temperature rise, t , as shown in 10.4.1.

13.2 *Thermochemical Corrections* (Appendix X1)—Compute the following for each test:

- e_1 = correction for the heat of formation of HNO_3 in Btu. Each millilitre of standard sodium carbonate is equivalent to 10.0 Btu,
- e_2 = correction for heat of combustion of ignition wire, Btu,
 - = 0.41 Btu/mm or 2.6 Btu/mg for No. 34 B & S gage Chromel C wire,
 - = 0.49 Btu/mm or 3.2 Btu/mg for No. 34 B & S gage iron wire, and
- e_3 = correction for difference between heat of formation of H_2SO_4 from the heat of formation of HNO_3 in Btu,
 - = 23.7 times percent of sulfur in sample times mass of sample in g.

14. Calorific Value (Note 10)

14.1 *Gross Calorific Value*—Calculate the gross calorific value (gross heat of combustion at constant volume), Q_g (gross), as follows:

$$Q_g (\text{gross}) = [(tE) - e_1 - e_2 - e_3]/g \quad (3)$$

where:

- Q_g (gross) = gross calorific value, Btu/lb,
- t = corrected temperature rise calculated in 13.1,
- E = energy equivalent calculated in 10.4.3,
- e_1, e_2, e_3 = corrections as prescribed in 13.2,

and

g = mass of sample, g.

14.2 *Net Calorific Value*—Calculate the net calorific value (net heat of combustion at a constant pressure), Q_p (net) as follows:

$$Q_p (\text{net}) = Q_g (\text{gross}) - 10.30 (H \times 9)$$

where:

- Q_p (net) = net calorific value, Btu/lb,
- Q_g (gross) = gross calorific value, Btu/lb, and
- H = total hydrogen, %.

NOTE 10—This calculation gives calorific value in Btu/lb. To obtain calorific value in J/g, see Appendix X2.

15. Report

15.1 The results of the calorific value may be reported on any of a number of bases, differing from each other in the manner that moisture is treated.

15.2 Use the percentage of moisture in the sample passing a No. 60 (250- μm), sieve (Test Method D 3173) to calculate the results of the analysis sample to a dry basis.

15.3 Procedures for converting the value obtained on the analysis sample to other bases are described in Method D 3180.

16. Precision and Bias

16.1 The following criteria should be used for judging the acceptability of results (95 % probability) on split 60-mesh (250- μm) sample.

16.1.1 *Repeatability*—Duplicate results by the same laboratory, using the same operator and equipment, should not be considered suspect unless they differ by more than 50 Btu/lb on a dry basis.

16.1.2 *Reproducibility*—The results submitted by two or more laboratories (different equipment, operators, date of test, and different portions of the same pulp) should not be considered suspect unless the two results differ by more than 100 Btu/lb on a dry basis.

16.2 *Bias*—There should be no bias because the equipment is standardized with a compound having a known heat of combustion.

TABLE 1 Calorific Values

1 Btu = 1055.06 J	1 Btu/lb = 2.326 J/g
1 Calorie ^a = 4.1868 J	1.8 Btu/lb = 1.0 cal/g

^a International tables calorie.

TABLE 2 Standard Deviations for Calorimeter Standardization^a

Standardization Number	Column A	Column B	Column C
	Energy Equivalent (Btu/lb) × (g/°C)	Code to 4400 (Column A - 4400)	(Column B) ²
1	4412	12	144
2	4407	7	49
3	4415	15	225
4	4408	8	64
5	4404	4	16
6	4406	6	36
7	4409	9	81
8	4410	10	100
9	4412	12	144
10	4409	9	81
SUM		92	940

$$\text{Average} = \bar{X} = \Sigma X/10 = (92/10) + 4400 = 4409$$

$$\text{Variance} = s^2 = \frac{\Sigma \text{Column C} - [(\Sigma \text{Column B})^2/n]}{n - 1} = \frac{940 - [(92)^2/10]}{9} = 10.4$$

$$\text{Standard deviation} = s = \sqrt{\text{variance}} = \sqrt{10.4} = 3.22$$

^a In this example the values of energy equivalent are typical for a calorimeter calibrated so that, if the energy equivalent is multiplied by the temperature rise in degrees Celsius per gram of sample, the calorific value of the sample will be obtained in British Thermal units per pound.

TABLE 3 Summary of Numerical Requirements

NOTE—Test values exceeding table limits require additional runs.^a

Number of Runs	Maximum Range of Results		Maximum Difference between \bar{X}_1 and \bar{X}_2 ^b	
	Btu/°C	Btu/°F	Btu/°C	Btu/°F
1	±6	±4
2	8	5	±4	±3
4	14	8	±3	±2
6	17	10	±2	±2
10	20	12	±1	±1

^a Values in this table have been rounded off after statistical calculation, and are therefore not precisely in a ratio from 1.8 to 1.0.

^b \bar{X}_1 = average of original standard. \bar{X}_2 = average of check runs.

ANNEX

(Mandatory Information)

A1. THERMOMETRIC CORRECTIONS

A1.1 Thermometer Corrections

A1.1.1 It is necessary to make the following individual corrections, if not making the correction would result in an equivalent change of 5.0 Btu or more.

A1.1.2 *Calibration Correction* shall be made in accordance with the calibration certificate furnished by the calibration authority.

A1.1.3 *Setting Correction* is necessary for the Beckmann thermometer. It shall be made in accordance with the directions furnished by the calibration authority.

A1.1.4 *Differential Emergent Stem Correction*—The calculation of differential stem correction depends upon the way the thermometer was calibrated and how it was used. Two conditions are possible:

A1.1.4.1 *Thermometers Calibrated in Total Immersion and Used in Partial Immersion*—This emergent stem correction is made as follows:

$$\text{Correction} = C_s = K (t_f - t_i) (t_f + t_i - L - T)$$

where:

C_s = emergent stem correction,
 K = 0.00016 for thermometers calibrated in °C,
 = 0.0009 for thermometers calibrated in °F,
 L = scale reading to which the thermometer was immersed,
 T = mean temperature of emergent stem,
 t_i = initial temperature reading, and
 t_f = final temperature reading.

NOTE A1.1—*Example:* Assume the point L , to which the thermometer was immersed was 16°C; its initial reading, t_i , was 24.127°C, its final reading, t_f , was 27.876, the mean temperature of the emergent stem, T was 26°C; then:

Differential stem correction, C_s
 = 0.00016 (28 - 24) (28 + 24 - 16 - 26)
 = + 0.0064°C.

A1.1.4.2 *Thermometers Calibrated and Used in Partial Immersion, but at a Different Temperature than the Calibration Temperature*—This emergent stem correction is made as follows:

$$\text{Correction} = C_s = K (t_f - t_i) (t_e - t_c)$$

where:

C_s = emergent stem correction,
 K = 0.00016 for thermometers calibrated in °C,
 = 0.0009 for thermometers calibrated in °F,
 t_i = initial temperature reading,
 t_f = final temperature reading,
 t_e = observed stem temperature, and
 t_c = stem temperature at which the thermometer was calibrated.

NOTE A1.2—*Example:* Assume the initial reading, t_i , was 80°F, the final reading, t_f , was 86°F, and that the observed stem temperature, t_e , was 82°F, and calibration temperature, t_c , was 72°F then:

Differential stem correction:
 = 0.00009 (86 - 80) (82 - 72)
 = 0.005°F

APPENDIXES

(Nonmandatory Information)

X1. THERMOCHEMICAL CORRECTIONS

X1.1 *Energy of Formation of Nitric Acid*—A correction, e_1 , (10.4.2 and 13.2), is applied for the acid titration. This correction is based on the assumptions (1) that all the acid titrated is HNO_3 formed by the following reaction: $1/2 \text{N}_2 (\text{g}) + 5/4 \text{O}_2 (\text{g}) + 1/2 \text{H}_2\text{O} (\text{l}) = \text{HNO}_3$ (in 500 mol H_2O), and (2) that the energy of formation of HNO_3 in approximately 500 mol of water under bomb conditions is minus 59.0 kJ/mol.¹

X1.1.1 A convenient concentration of Na_2CO_3 is 0.394 N (20.9 g Na_2CO_3 /1000 mL) which gives $e_1 = 10$

times V , where V is the volume of Na_2CO_3 in milliliters. The factor 10.0 ($0.394 \times 59.0 = 2.326$) is to be used for calculating calorific value in Btu/lb. For other units see Table X2.1. When H_2SO_4 is also present, a part of the correction for H_2SO_4 is contained in the e_1 correction and remainder in the e_2 correction.

¹ Calculated from data in National Bureau of Standards Technical Note 270-3.



X1.2 Energy of Formation of Sulfuric Acid—By definition (see Definitions D 121) the gross calorific value is obtained when the product of the combustion of sulfur in the sample is SO_2 (g). However, in actual bomb combustion process, all the sulfur is found as H_2SO_4 in the bomb washings. A correction, e_2 (see 13.2) is applied for the sulfur that is converted to H_2SO_4 . This correction is based upon the energy of formation of H_2SO_4 in solutions, such as will be present in the bomb at the end of a combustion. This energy is taken as -295.0 kJ/mol.⁹ A correction of 2 times 59.0 kJ/mol of sulfur was applied in the e_1 correction, so the additional correction necessary is $295.0 - (2 \text{ times } 59.0) = 177$ kJ/mol, or 5.52 kJ/g of sulfur in the sample (55.2 J times weight of sample in grams times percent sulfur in sample). This causes e_2 to be 23.7 times weight of sample in grams times percent sulfur in sample. The factor 23.7 (equals 55.2/2.326), for e_2 (see 13.2) is to be used for calculating calorific value in Btu/lb. For other units, see Appendix X2. The values above are based on a coal containing about 5 % sulfur and about 5 % hydrogen. The assumption is also made that the H_2SO_4 is dissolved entirely in the water condensed during combustion of the sample.

X1.2.1 If a 1-g sample of such a fuel is burned, the resulting H_2SO_4 condensed with water formed on the walls of the bomb, will have a ratio of about 15 mol of water to 1 mol of H_2SO_4 . For this concentration, the

energy of the reaction SO_2 (g) + $\frac{1}{2}$ O_2 + H_2O (l) = H_2SO_4 (in 15 moles of H_2O) under the conditions of the bomb process is -295 kJ/mol.⁹ Basing the calculation upon a sample of comparatively large sulfur content reduces the possible overall errors, because, for small percentages of sulfur, the correction is smaller.

X1.3 Fuse (Ignition) Wire—Calculate the energy contributed by burning the fuse wire in accordance with the directions furnished by the supplier of the wire. For example, the energy of the combustion of No. 34 $\frac{1}{8}$ & S gage Chromel C wire is 6.0 J/mg or approximately 0.95 J/mm. For calculating e_2 for use in Eqs 2 and 3, these give $e_2 = 0.41$ times length (mm) of wire or $e_2 = 2.6$ times weight (mg) of wire. The energy required to melt a platinum wire is constant for each experiment if the same amount of platinum wire is used. As the energy is small, its effect is essentially cancelled out in the relationship between the standardization experiments and the calorific value determinations, and it can be neglected. The factors listed above for e_2 (10.4.2 and 13.2) are suitable for calculating calorific value in Btu/lb. For other units, see Appendix X2.

⁹ Calculated from data in National Bureau of Standards Circular 500.

⁹ Mott, R. A. and Parker, C. "Studies in Bomb Calorimetry IX—Formation of Sulfuric Acid", *Fuel*, FUEL B, Vol. 37, 1958, p. 371.

X2. REPORTING RESULTS IN OTHER UNITS

X2.1 Reporting Results in Joules per Gram:

X2.1.1 The gross calorific value can be expressed in joules per gram, calories per gram, or British thermal units per pound. The relationships between these units are given in Table 1.

X2.1.2 Because the energy of combustion of the reference material is measured and certified by the National Bureau of Standards in joules per gram, the most straightforward usage of the reference material would lead to the calorific value of the fuel in joules per gram. To carry out this procedure, we make changes outlined in X2.1.3 through X2.1.5.

X2.1.3 For calculating energy equivalent, substitute Eq 2' for Eq 2:

$$E = [(H'g) + e_1']/t \quad (2')$$

where the meanings of the symbols in Eq 2' are the same as in Eq 2 except that:

E' = energy equivalent in units of joules per temperature unit,

H' = the heat of combustion of reference material in units of joules per gram weight in air (J/g from the certificate for the NBS benzoic acid), and

e_1' and e_2' = corrections in units of joules, (see Table

X2.1).

X2.1.4 For calculating gross calorific value, substitute Eq 3' for Eq 3:

$$Q_g (\text{gross}) = [(Q_g') - e_1' - e_2']/g \quad (3')$$

where the meanings of the symbols in Eq 3' are the same as in Eq 3 except that:

$Q_g (\text{gross})$ = gross calorific value with units of joules per gram (weight in air),

E' = energy equivalent units, of joules per temperature unit, and

e_1' , e_2' , and e_3' = corrections in units of joules (see Table X2.1).

X2.1.5 Precision:

X2.1.5.1 Repeatability—Duplicate results by the same laboratory, using the same operator and equipment, should not be considered suspect unless they differ by more than 120 J/g.

X2.1.5.2 Reproducibility—The results submitted by two or more laboratories (different equipment, operators, date of test, and different portions of the same sample) should not be considered suspect unless the results differ by more than 240 J/g.

TABLE X2.1 Alternative Thermochemical Correction Factors (Units in Joules)^a

Correction	Multiplication Factor	Multiply By
c_1' (HNO ₃)	20 J/mL	mL of 0.34 N Na ₂ CO ₃
c_1' (H ₂ SO ₄)	55.2 J/cgS	percentage of sulfur in sample times mass of sample in grams
c_2' (fuse wire)	0.95 J/mm	length (mm) of No. 34 B & S gage Chromel C wire
or		
c_2' (fuse wire)	1.14 J/mm	length (mm) of No. 34 B & S gage iron wire
c_3' (fuse wire)	6.0 J/mg	mass (mg) of Chromel C wire
or		
c_3' (fuse wire)	7.4 J/mg	mass (mg) of iron wire

^a To be used in Eqs 2' and 3' only.

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J.S. Environmental Protection Agency
CLP Sample Management Office
P. O. Box 818, Alexandria, Virginia 22313
PHONE: (703)/557-2490 or FTS/557-2490

TO C IN SOIL

SAS Number

SPECIAL ANALYTICAL SERVICES
Client Request

☒

Regional Transmittal

☐

Telephone Request

- A. EPA Region/Client: Region V WW Engineering & Science
- B. RSCC Representative: Jan Pels
- C. Telephone Number: (312) 353-2720
- D. Date of Request: _____
- E. Site Name: Skinner Landfill - West Chester, Ohio

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. General description of analytical service requested: Determination of organic carbon (%)
in soil (air-dried-all screened through 100 or 140 mesh). Applicable concentration 0.1%
to 10.0 % or more. Detailed information must be provided with Case Narrative for test pro-
cedures, instrumentation/apparatus and QC used. See Attachment 1.
2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium, or high concentration): 80 low soil and 48 low
sediment samples.

Includes duplicates and blanks.

3. Purpose of analysis (specify whether Superfund (Remedial or Enforcement), RCRA, NPDES, etc.):
Superfund, Remedial Action

- 1

I. DATA REQUIREMENTS

<u>Parameter:</u>	<u>Detection Limit</u>	<u>Precision Desired</u> (% or Conc.)
<u>Organic Carbon % in</u>	<u>0.10%; report actual</u>	<u>± 20%; on duplicate</u>
<u>Soil</u>	<u>detection limit if</u>	<u>sample results</u>
<u></u>	<u>smaller</u>	<u></u>
<u></u>	<u></u>	<u></u>
<u></u>	<u></u>	<u></u>
<u></u>	<u></u>	<u></u>
<u></u>	<u></u>	<u></u>

II. QC REQUIREMENTS

<u>Audits Required</u>	<u>Frequency of Audits</u>	<u>Limits* (% or Conc.)</u>
1 <u>Prep. Blanks</u>	<u>1 in every 10 samples</u>	<u>≤0.1%</u>
2 <u>Duplicate Samples</u>	<u>1 in 5 samples</u>	<u><20% RPD in differences</u>
		<u>of duplicate sample</u>
		<u>results, or <0.2%</u>
		<u>differences at small</u>
		<u>concentrations.</u>
3 <u>Positive Control (to be</u>	<u>1 in 10 samples</u>	<u>88-115% recovery</u>
4 <u>determined by the lab)</u>		
<u>Instrument Calibration</u>	<u>1 in 10 or fewer samples</u>	<u>90-110% recovery for</u>
<u>Checks and Calibration</u>		<u>calibration check, and</u>
<u>Blanks (if appropriate)</u>		<u><0.1% total carbon for</u>
		<u>assumed routine</u>
		<u>sample weight</u>

III. ACTION REQUIRED IF LIMITS ARE EXCEEDED:

Take corrective action and repeat analysis.

Jan Pels 312/ 353-2720 or Chuck Elly (312) 353-9087

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for special analytical services. Should you have any questions or need any assistance, please call the Sample Management Office.

ATTACHMENT I

--- Determination of organic carbon(%) in soil, using sub-aliquots of air-dried soil, passed through a 100 mesh to 140 mesh screen. All of the sub-aliquot must pass the screen. Applicable organic carbon concentration range of interest is 0.1% to 10% (or larger) in soil, (dry weight basis). Laboratory may report lower concentration values.

Test procedures used for determining soil shall be the 1) Dry combustion (resistance furnace), 2) Dry combustion (induction furnace), 3) Dry combustion (automated methods), or 4) Wet combustion (combustion train) methods of analysis specified by Table 29-1 of "Methods of Soil Analyses," Part 2 - Chemical and Microbiological properties, 2nd ed., 1982, American Society of Agronomy, and Soil Science Society of America, Madison, Wisconsin. Copies of this copyrighted material are not being provided, because no laboratory doing organic carbon analysis of soil should be without it.

Any automated dry combustion test procedure used must provide results consistent with the other 3 methodologies and must be consistent with the requirements of Chapter 29, Sections 29-1, 29-2, and 29-3, "Methods of Soil Analysis" (MSA) Part II, 2nd ed., as appropriate. Soils can be calcerous or noncalcerous soils, with varying amounts of organic carbon. Soils determined may be subsurface as well as surface soils. If peat or muck soils are ever encountered, the laboratory will provide with the case narrative, limitations of any sample results and any solutions to problems encountered. This is also true for any other problem sample types encountered.

The laboratory, providing organic carbon analysis data, will provide information with the case narrative concerning methodology, instrumentation, and specific QA practices used for the set of soils tested. Requested information is detailed in items #8, and #9 of this SAS.

ATTACHMENT 7
Analytical Methods - Organic-Carbon in Soil

- 7a. Sample Preparation: Representative sub-aliquot of air-dried soil (see % solids SAS) screened through 100 or 140 mesh as appropriate. All of the sub-aliquot must pass this screen.
- b. Test for Presence of Inorganic Carbon, MSA, Part II, Section 29-3.3.1. Place finely ground soil on a spot plate, and moisten with a few drops of water. Add 4 N HCl dropwise to the wetted sample and observe any effervescence. Allow sufficient time for dolomite to react (~5 min). If inorganic carbon is absent proceed with Total Carbon in items #7c, or 7d below. If inorganic carbon is present, or the test is not definitive, proceed with items #7e, 6F #7f prior to Total Carbon measurements of Item #7c or #7d.
- c. Total Carbon (Dry Combustion), MSA, Part II, Section 29-2.2.2. Use this as a guide for instrumental specifications. Instrument must test solid sample directly. Illustrative examples of this methodology are:
- 1) Total Carbon (Dry Combustion - Medium Temperature Resistance Furnace), MSA, Part II, Section 29-2.2.3.
 - 2) Total Carbon (Dry Combustion - High Temperature Induction Furnace), MSA, Part II, Section 29-2.2.4.
 - 3) Total Carbon (Dry Combustion - Other Instrumental Methods), MSA, Part II, Section 29-2.2.5. Any other instrumentation such as this must be justified and provide results as precise and accurate as the results from Sections 29-2.2.3, and 29-2.2.4.
- d. Total Carbon (Wet Digestion), MSA, part II, Section 29-2.3.2 Soil digested in 60:40 mixture of sulfuric acid and phosphoric acid (containing $K_2C_2O_7$). CO_2 evolved is absorbed and weighed, or absorbed in standard base and titrated.
- 1) Specific examples are found in MSA, Part II, Figure 29-2, Figure 29-3, and Section 29-2.3.3.
- e. Pretreatment prior to Dry Combustion, MSA, Part II, Section 29-3.3.3. Inorganic carbon is removed by treating sample in a combustion boat, with 5% sulfurous acid (H_2SO_3). After several hours, remove the excess H_2SO_3 by leaving overnight in an evacuated dessicator. Read citation for further details.
- f. Pretreatment prior to Wet Digestion, MSA, Part II, Section 29-3.3.2. Inorganic carbon is removed by sulfuric acid - ferrous sulfate reagent in apparatus used for total carbon (Wet Digestion) prior to Total Carbon measurement. See citation for further details.

ATTACHMENT 7 (Cont.)

- g. Use only the methods specified above or obtain approval of CPMS, CRL prior to use of other method. Test procedure description, and description of specific measurement principles including equivalency to each of the 10 items of Figure 29-1 of MSA, part II and sample pretreatment of Section 29-3, MSA, Part II.**
- h. Laboratory performing Total Carbon determinations must use and have a recognized procedure for removal of any inorganic carbon in sample.**

ATTACHMENT 8

A variety of apparatus, instrumentation, sample preparation systems and read-outs can be used. It is the responsibility of the laboratory to provide appropriate QC audits and QC data with each set of samples tested.

If instrumentation requires calibration, provide calibration curve, including zero concentration standard and preparation blanks. Provide positive control (a test sample prepared independently from calibration standards) that provides a measure of accuracy of system. This should be done for all systems including gravimetric read-outs.

ATTACHMENT 9
Analytical Results Required

As part of Case Narrative, attach description of test procedure and instrumentation used for measurement of Total C and removal of any Inorganic C. Test procedure description must include sufficient information that the nature of specific analytical result deliverables can be determined including QC audits. In Case Narrative, discuss any problem type samples (including peat or muck soils), limitations on any sample results, and solution taken to resolve any problems. A sample preparation log will be provided, as appropriate.

Bench record tabulating any order of any sample weights and tare weights of absorbed CO₂, instrument calibrations, blanks, QA audits, etc., must be provided along with copies of any worksheets used to calculate results. Include copies of any instrument readouts. All must be legible. Report results as % organic Carbon on a dry weight basis (103-105°).

APPENDIX E

STANDARD OPERATING PROCEDURES
FOR
FIELD EQUIPMENT

STANDARD OPERATING PROCEDURES
FOR
IN-SITU HYDRAULIC CONDUCTIVITY SLUG TESTS

STANDARD OPERATING PROCEDURES IN-SITU HYDRAULIC CONDUCTIVITY FIELD MEASUREMENT PROCEDURES

General

Hydraulic conductivity can be estimated by a variety of techniques. One of the most common techniques is to subject a monitoring well to a stress by changing its water level and then monitoring how the water level responds to this stress. To perform a slug test (in-situ hydraulic conductivity test), a known quantity of water is injected (or removed) "instantaneously" into the well. After the water has been injected, the water level is monitored as it returns to the original static water level.

Of the various methods for stressing the water level in a well, WW Engineering and Science has found that application of a vacuum which draws water into the well is very efficient. After a constant vacuum can be released, creating the effect of an instantaneous slug. It should be noted that in some applications, it may be more desirable to apply pressure rather than a vacuum due to the static water level in the well.

Equipment Needed

- Hermit Data Logger
- 10 psi Pressure Transducer
- Air Cadet Pressure/Vacuum Station
- Valves, Pipe Fittings, etc for well head
- Pipe Wrenches
- Stainless Steel Measuring Tape
- 12-Volt Battery

Before going into the field, information regarding the well diameter and casing material should be known to be sure the in-situ kit contains the proper adapter for use with the wells to be tested. Within the plastic container used to hold the equipment, there should be adapters for 1-1/4", 2" and 4" diameter wells; PVC or galvanized casing; threaded or unthreaded caps.

Procedure

1. Measure Static Water Level.
2. Record well number, date, time, water level, overall well depth, and test number and step number of Hermit.

3. Mount valves and fittings on well head.
4. Position pressure transducer approximately 5 to 8 feet below water level (15 to 17 feet if pressure is to be applied to the well). Depth can be estimated when lowering cable into well.
5. Connect Hermit cables between Hermit and transducer.
6. Install rubber fittings around transducer cable to insure an air-tight connection.
7. Connect clear tubing between Air Cadet pressure/vacuum station and well head fitting.
8. Reference Hermit to zero using the following procedure.

The reference **LEVEL** mode is used to convert PSI values obtained with a pressure transducer to water levels. This mode must not be used with any other type of transducer. The parameters listed in the menu allow a wide variety of transducer ranges and water level data display modes.

Use the **SCAN DOWN** Key to move the display towards the bottom of the menu; **SCAN UP** to move the display towards the top of the menu. **STOP/NEXT** will exit the menu and return to the status display. Press **ENTER** to modify the displayed parameter for the selected input.

NOTE: The high and low limit alarm parameters will not be presented if the alarm output option has not been installed.

Reference Hermit (continued)

To modify the reference level, press ENTER when the display shows the reference parameter.

The current value of the reference level is displayed with the leftmost digit blinking. Use the SCAN and STOP/NEXT keys to change the digits to their correct values.

Press ENTER to set the new value. The display returns to the transducer menu.

The reference level parameter is used to reference the transducer readings to a known initial condition. In hydrologic applications, this allows top of casing and surface water values to be derived from transducer head readings. The transducer must be connected to the instrument and placed at its initial depth before entering the reference level. If absolute level values are not important and only changes in level are required, the reference level must be set to zero. All water level display modes require that the reference level be entered for proper operation.

To modify the transducer scale factor press ENTER when the display shows the scale parameter.

Reference Hermit (continued)

The current value of the scale factor is displayed with the leftmost digit blinking. Use the SCAN and STOP/NEXT keys to change the digits to their correct values.

- 9.0 Conduct a Pre-Run Checkout and make a note of the initial transducer value in the following manner.

It is very important to check the operation of the unit before starting a test. A quick reading taken on each active input ensures that all cables are connected and that the transducers are properly set to their pre-run conditions.

Start from the status display. A transducer can be read in any test mode.

Press the XD key. If two inputs are active, the input number is displayed with a blinking digit. Use the SCAN keys to change the input number to the desired value. STOP/NEXT will abort the selection and return to the status display. Press ENTER to select the input. This prompt is skipped if only one input is active.

Pre-Run Checkout (continued)

The unit takes a reading and displays the transducer value...

... then returns to the status display.

A dual mode reading takes about 12 seconds...

... the primary parameter is displayed...

... Then the temperature in degrees centigrade...

... then returns to the status display.

NOTE: When the level mode is selected and the unit is idling or waiting for a delayed start, the transducer depth (head) is displayed instead of the water level. This allows the operator to properly set the transducer below the largest expected drop in water level.

10. Connect wires from Air Cadet to 12-volt power supply.
11. Allow pressure/vacuum to stabilize within well. Well is stable when transducer value remains fairly consistent for 25 to 30 seconds. This value should, in theory, equal initial transducer value, but may not due to leaking well fittings, etc.
12. Close valve on pressure/vacuum line.
13. Immediately after closing valve, start Hermit in the following manner.

Starting a Test

Start from the status display with all test and transducer parameters set. A test can only be started from the idle mode.

Press the START key. If the unit is in the wrong mode, "Error" will be displayed. The "Er:LOG" message is displayed if logarithmic sampling is selected with a dual mode transducer.

The selected test number is displayed...

Starting a Test (Continued)

... then the top selection from the start menu. Press **SCAN DOWN** to select the delayed start mode; **SCAN UP** to select immediate start. Press **STOP/NEXT** to cancel the start function without collecting data. Press **ENTER** to select the displayed start type.

NOTE: Pressing the **START** key does **NOT** begin data collection; it only initiates the preparation to start procedures.

To perform an immediate start, press **ENTER** when the display shows the immediate start selection.

If the linear sampling mode has been selected, the display returns to the status display.

During the first ten minutes of log mode, the unit displays the log cycle. Only the **STOP** functions is active until...

... the display returns to the status display.

Starting a Test (continued)

The normal sleep delay of thirty seconds is extended to ninety seconds to simplify synchronizing the immediate start to an external event.

To set up a delayed start, press ENTER when the display shows the delayed start selection.

The current date is displayed with the leftmost digit flashing. Use the SCAN and STOP/NEXT keys to change the digits to the delayed start date. Press ENTER to set the delay date.

If the date setting is valid, the current time is displayed with the leftmost digit flashing. Use the SCAN and STOP/NEXT keys to change the digits to the delayed start time. Press ENTER to set the delay time.

The delayed start date and time must meet the same criteria as an internal clock setting.

If the time setting is valid, the display returns to the status display. The unit will automatically perform the start function (as outlined for immediate start) at the programmed date and time.

14. As soon as test begins, the Hermit will display "LOG 1". As soon as this is displayed, open large valve.
15. Vacuum pump may now be shut off.
16. Allow water level to return to initial static water level. The water levels cannot be read for the first ten minutes of a test; after that the data can be displayed using the following procedure:

Displaying Data

Start from the status display. Data may be viewed in any test mode.

Press the DATA key. The unit will blink the current test number. Use the SCAN keys to change the test number to the desired value. STOP/NEXT will abort the selection and return to the status display. Press ENTER to select the test for display.

The selected test number must be in the range zero to the currently active test.

Displaying Data (continued)

The active test has not been run and contains no data.

If more than one input is active select the input to be displayed and press ENTER. If only one input is active, this prompt is skipped.

If more than one step has been used, the highest step number is displayed. Select the step number to display and press ENTER. This prompt is skipped if no steps have been used.

The unit then displays the elapsed time in minutes of the last sample point...

... then the sample point value in the selected units.

Displaying Data (continued)

If a dual mode transducer is selected, the unit will then display the temperature in degrees centigrade.

Use the SCAN DOWN key to display earlier data points; the SCAN UP key to display later data points. STOP/NEXT will abort the data display and return to the status display. Holding down the ENTER key and pressing a SCAN key will cause the unit to scan up or down by ten data points. Each time a SCAN key is pressed, the display shows the elapsed time in minutes and the data point value.

To view data from the start of the test or step, press the START key. The display shows the start date...

... the start time...

... moves to time $T = 0$...

... then displays the data at $T = 0$.

Display Data (continued)

NOTE: Elapsed time values for the first two seconds of log mode data will appear somewhat ambiguous due to the display's inability to show small decimal values. Elapsed time up to two minutes cannot be displayed with full resolution. Use the following table to convert the displayed times to their full resolution.

17. After water level has stabilized, stop Hermit test and remove everything from well. To stop a Hermit test, use the following procedures:

Stopping a Test

Start from the status display with the unit in an active data collection mode. Hold down the ENTER key and press the STOP/NEXT key.

The "Error" message is displayed if the unit is already stopped and is in the idle mode.

Otherwise the stop prompt is displayed with an underline cursor flashing. Press STOP/NEXT to cancel the stop selection; ENTER to confirm the selection.

When the stop function is confirmed, the unit returns to the status display.

Stopping a Test (continued)

NOTE: During the first ten minutes of log mode data collection the stop function acts immediately with no opportunity to confirm or cancel the selection.

Additional Comments

Additional steps are required if more than ten tests are to be run before transferring the data to the IBM. Rather than stopping the test (Step 16), simply unplug transducer and proceed as above. This will cause the Hermit to continue to process data while moving to the next well. The procedure at the next well will be the same as outlined above, with the exception that the Hermit cannot be referenced to zero; rather than starting the test (Step 13), the test must be stepped using the following procedure:

Stepping a Test

A step can only be started when the unit is in the run mode.

Press the START key. "Error" will be displayed if the unit is in the wrong mode, if the last step (4) is already running, or if there is insufficient memory to start the next step

Otherwise the next step number is displayed...

Stepping a Test (continued)

... Then the top selection from the start menu. The start menu options are identical to those for starting a test.

NOTE: When a delayed start is programmed for a step, data collection will stop for the previous step. The unit will not collect further data until the delayed start time.

The Hermit is capable of handling Step 0 through 4 for each test; therefore, it expands the capability of the Hermit to 50 slug tests. It is not recommended to store that many tests in the Hermit because if the operator should make a small error in running the Hermit, it could erase all the tests.

If the static water level is within 5 feet of top of casing, it is recommended that pressure be applied rather than a vacuum. This is due to the fact that the vacuum might pull the water up into the Air Cadet and possibly damage the pump seals.

The pressure or vacuum release valves should be set at the proper setting to allow for 3 to 5 feet of water level change. If not, refer to Air Cadet owner's manual to change settings.

If the ambient temperature is greatly different than ground water temperature (above 80°F or below 30°F) about ten minutes should be allowed so that the pressure transducer can stabilize after it has been lowered into the ground water.

DATA INTERPRETATION

Data Transfer

Data are transferred from Hermit to the IBM via the RS-232 port using a menu-driven software package from In-Situ, Inc.

After data is computed, PC-Write is used to edit the file, so that it is in the proper form to import to a lotus file. This requires removing all of the data headings, and removing the two spaces between the minus sign and the numbers. This edited file is saved as a ".prn" file so it can be imported into Lotus.

Lotus 1-2-3 is used to manipulate the data. Transducer values need to be corrected to display differences from static water levels. Time values are corrected so it begins at the start of the test (transducer value changes dramatically). Data are manipulated and graphed using Lotus.

Methods:

An understanding of the subsurface conditions is a prerequisite to proper interpretation of test results. This includes knowledge of the type of geologic materials being tested, the thickness of the test zone, the type of geologic materials overlying and underlying the test zone, and the position of the well screen within the test zone. In addition, the physical dimensions of the well must be known.

Method 1:

The Bouwer and Rice (1976) solution to water level decay after stress is applicable to unconfined conditions, but the authors note that the technique is applicable to confined aquifers if the water enters the aquifer through the upper confining layer through compression or leakage. Their equations are based on a modification of the Time equation and assumes:

1. Drawdown of the water table around the well is negligible.
2. Flow above the water table can be ignored.
3. Head losses as water enters the well are negligible.
4. The aquifer is homogeneous and isotropic.

The equations of importance are:

$$K = [r_c^2 \ln(R_e/r_w) \ln(Y_o/Y_t)] / [2 lt]$$

and (for partially penetrating wells):

$$\ln(R_e/r_w) = \left[\frac{1.1}{\ln(h/r_w)} + \frac{A + B \ln[(D-h)/r_w]}{l/r_w} \right]^{-1}$$

Where:

- l = screen length
- Y_o, Y_t = water level, static, and at time t
- R_e = effective radius over which Y is dissipated
- r_c = radius of casing
- r_w = horizontal distance from well center to original aquifer
- t = time between measurements
- H = distance between static water level and base of screen
- D = aquifer thickness
- A, B = dimensionless coefficients that are a function of l/r_w and determined graphically

Values of time and water level are selected from the straight-line portion of the plot of water level (log scale) versus time (arithmetic scale). These values plus the values for well construction and aquifer thickness are substituted into the above equations to determine horizontal hydraulic conductivity.

Method 2:

Hvorslev (1951) noted that flow of water to or from an observation well will take place until the pressure differential between the formation and the well are eliminated. The time required for equalization of pressure is defined by Hvorslev as the basic lag time (designated T). The magnitude of the time lag is dependent upon well construction and is inversely proportional to permeability. The basic time lag is determined graphically from a plot of residual hydraulic head (log) versus time (arithmetic).

Hvorslev presented equations to calculate permeability from test results using various types of observation wells. A technique commonly used by WW Engineering and Science is Hvorslev's Case G, where the observation well screen is installed within an aquifer and confining strata are far above or below the screen.

In this case, horizontal permeability is defined by:

$$k_h = [d^2 \ln(2 ml/D)] / [8 lT]$$

Where:

d = diameter of well casing
l = length of openings in well screen
D = diameter of well screen
m = transformation ratio; $m = (k_h/k_v)$
T = basic lag time
 k_h = horizontal permeability
 k_v = vertical permeability

Hvorslev's equations require values for the ratio of horizontal versus vertical permeability; but since this is rarely known, the ratio is estimated. The reader should refer to the original texts of the authors referenced for more details on applicability of these tests.

REFERENCES

- Bouwer, H. and R.C. Rice, 1976. A slug-test for determining hydraulic conductivity of unconsolidated aquifer with completely or partially penetrating wells: *Water Resources Research*, Vol. 11, No. 3, pp. 423-428.
- Hvorslev, M.J., 1951. Time lag and soil permeability in ground water observation: US Corps of Engineers, Waterways Exp. Station, Bulletin 36, p. 50.

STANDARD OPERATING PROCEDURE
FOR MEASURING
SPECIFIC CONDUCTIVITY WITH
YSI MODEL 32

**Standard Operating Procedure for
Field Determination of Conductivity, Method 205**

Groundwater, Surface Water, and Wastewater

1.0 Method Summary

- 1.1** Conductivity is a numerical expression on aqueous solution's ability to carry an electric current. This is dependent on the presence of ions, their concentrations, mobility, valence, and on the temperature of the solution.
- 1.2** The conductivity probe is immersed in a sample and the conductivity is read directly off of the meter scale.

2.0 Interferences

- 2.1** Temperature greatly influences the electrolytic conductivity of a sample. therefore, it is extremely important accurate temperature measurements are made.

3.0 Instrumentation

- 3.1** Conductance meter YSI Model 32.

4.0 Materials and Reagents

Conductivity cell
Thermometer
Specimen containers

5.0 Standard

5.1 Primary Working Standard:

Potassium chloride standard 0.01N: dissolved 0.7456 g anhydrous KCl in deionized water and dilute to 1 liter at 25°C. Conductivity = 1,413 umhos/cm.

6.0 Calibration

- 6.1 Check the conductivity of the standard prior to actual sample evaluation. Record the temperature of each standard.
- 6.2 Calculate the conductivity at 25°C making adjustments for the temperature, see 8.1 for equation.

7.0 Procedure

- 7.1 Rinse the cell with deionized water.
- 7.2 Measure the conductivity of each sample by swirling the cell in a portion of the sample. Record the conductivity reading and the temperature. Collect three conductivity readings until the readings are within ± 5 umhos/cm.
- 7.3 Calculate the conductivity at 25°C as outlined in Section 8.1.

8.0 Calculations

8.1 Conductivity at 25°C = $\frac{K}{1 + 0.0191(t-25)}$

K = measured conductivity
t = temperature of sample, °C

9.0 Quality Control

- 9.1 Document all calibrations and verification of readings including time and meter readings.
- 9.2 A blank of deionized water is run and should have a conductivity of less than 5 umhos/cm.
- 9.3 The initial standard is checked in between samples.

STANDARD OPERATING PROCEDURES

FOR

HNU MODEL PI 101

Standard Photoionization Detector (PID)

Operations and Procedures

Introduction

The Hnu model PI 101 is designed to measure the concentration of trace gases in the atmosphere. The principle of photoionization detection (PID) is employed. A sensor, consisting of a sealed ultra-violet light source (either 9.5 eV, 10.2 eV, or 11.7 eV) emits photons energetic enough to ionize many trace species of organic hydrocarbons. The ionized gases are in turn detected by a collector electrode where the current is measured and converted to a ppm value. The useful range of the instrument is from a 1 ppm to 2,000 ppm. This instrument is used frequently by WW to evaluate ambient air quality for health and safety purposes or to detect the presence of volatile organic hydrocarbons in soil and sediment samples.

Operation

1. Turn the function switch to the "battery check" position. The needle on the meter should read within the green area (battery area) of the scale; if not, the battery should be recharged.
2. Turn the function switch to the "on" position. Look into the end of the probe and confirm the purple glow of the UV lamp.
3. Zero the instrument; turn the function switch to the "standby" position and rotate the zero potentiometer until the meter reads zero. Clockwise rotation = upscale deflection; no calibration gas is necessary for this adjustment. Confirm zero reading is stable; if not, readjust.
4. Calibrate the instrument; turn the function switch to the proper measurement range (specific to the calibration gas). Connect the sensor to the provided cylinder of calibration gas, open the valve on the cylinder. Use the span control to adjust the instrument scale reading to the ppm value specified on the cylinder of calibration gas. The instrument is now ready for use. Be sure to position the function switch to "stand-by" between observations to prevent unnecessary drain on the battery.
5. To prevent the undetected escape of volatile vapors when scanning split spoon soil or sediment cores, have the instrument at the ready when the split spoon is opened.

Immediately upon opening the corer or split spoon, disturb the sample and scan representative areas of the sample.

- 6. The battery should be recharged each night. To charge the battery, place the mini-phone plug into the jack prior to plugging in the 120 VAC. When disconnecting the charge, remove from the 120 VAC before removing the mini-phone plug. Check the battery to confirm its charge.**
- 7. If the probe is held near AC power lines or transformers, an error may be observed. If AC "pick-up" is going to be a problem, the meter, in "stand-by" position, will indicate the magnitude of the error rather than reading zero. This may be taken into consideration and the error compensated for by simply subtracting the value observed when the instrument was on stand-by from the observed detected value when making a positive reading.**
- 8. The HNu PID is affected by humidity. It will not function properly in rainy weather, and "negative" deflection and difficulty with zeroing the instrument can occur under otherwise humid conditions.**

STANDARD OPERATING PROCEDURE

FOR

**KECK GEOPHYSICAL LOGGER
GAMMA LOGGING**

Keck SR-3000 Gamma Logger Standard Operating Procedure

1.0 Operating Instructions

The Keck SR-3000 Logger can be used to measure the natural gamma emissions within a borehole. The unit is designed to detect the presence of gamma radiation emitted primarily from radioactive potassium (K40).

1.1 Instrument Description

The instrument is designed to be carried in a truck or large vehicle and is made up of three primary units; the cable reel, the control console, and the logging probe. The cable reel contains 1500 feet of cable along with a 12 volt clutch-driven motor, depth indicator, and connector. The control console contains the logger speed, module select, recorder sensitivity, and power switches. Also the console has two analog recorders with independent base line zero adjustments. Instrument modules are required for each logging tool and plug into the control console.

1.2 Initial Set-Up Procedure

Connect the three interfacing cables between the control console and the cable reel. The cables should be connected as numbered on the units. Connect the two power cables to the control console and then connect the end clips to a 12 volt DC power supply making sure that the main power switch is off prior to the power hookup.

The next step is to position the system controls as follows:
(Refer to Figure 1 for the system controls location)

<u>Switch</u>	<u>Item No.</u>	<u>Setting</u>
Main power	1	off
Logging direction	5	off
Logging speed control	6	fully counterclockwise
Zero adjust	13 & 15	fully counterclockwise
Module selector switches	7 & 8	off: center position
Recorder channel sensitivity	9 & 10	1
Module Power	20	off
Depth counter	14	0000.0
Chart speed	21	5

1.2.1 Gamma Logging Setup

After the controls have been correctly positioned the gamma logging module should be inserted into either one of the module slots as shown in Figure 1. Next, the gamma ray sonde or logging tool should be connected to the cable reel connector. This may require the reeling of some cable out of the cable reel. To do this first turn on the main power switch, switch the logging direction switch to "down", and then slowly turn the speed adjust control knob. The vehicle should be turned on during logger operation. The connector and the tool should be mated by aligning the 4 pins, making sure that the larger pin is aligned with the larger hole. The connector is then slid together, and the threaded cover should be screwed down securely.

The next step is to place the sonde in the borehole. The cable should be placed on the well cable pulley unit or a suitable substitute to prevent cable wear. Lower the cable until the connector (top of the sonde) is at ground surface.

If the vehicle's 12-volt battery is being used, the vehicle should be turned on during logger operation.

At this point, the gamma module is in one of the available slots and the main power should be on. The instrument controls should be set as follows:

<u>Switch</u>	<u>Item No.</u>	<u>Setting</u>
Main power	1	on
Logging direction	5	off
Speed adjust control	6	fully counterclockwise
Zero adjust	13 & 15	fully counterclockwise
Module selector switches	7 & 8	right or left(1)
Recorder channel sensitivity	9 & 10	1
Module power	20	on
Depth counter	14	0000.0
Chart speed		5
Module adjustments		
Time constant	18	5
Sensitivity		1K

(1) Depending on the module position

1.2.2 Zeroing

First make sure that both of the module selector switches are switched to the correct location, depending on which slot the gamma module has been inserted. Hold the zero button down with the pens in the up position and wait until the pen locations stabilize. Then use the zero adjust knobs (13 & 15) to position the pens at the left hand edge of the chart scale. At this point it is a good idea to remove the pen covers.

1.2.3 Depth Setting

Rotate the metal sheave on the cable unit by lifting and rotating until the depth indicator displays -1.9. this position corresponds to the depth of measurement of this sonde, assuming the top of the sonde is at ground surface. Now adjust the paper position until the pens are at a depth of 1.9 feet (approximately 2 small squares). Mark a reference depth on the paper.

1.2.4 Logging

Now lower the pens onto the paper, do not lower the pens to the lowest position, just lower them until they firmly contact the paper. Typical gamma readings for unconsolidated sediments range from 100 to 2000 counts per minute. Set the left channel sensitivity on .2 and the right channel sensitivity on .5. These two settings should be a good starting point, but if additional information on the geology is available these starting positions can be varied.

Switch the logging direction switch to "down" and rotate the logging speed control knob until the cable speed indicator reads between 10 and 15 feet per minute.

The downhole log is typically used for adjustment, and the sensitivities and time constant can be varied until a satisfactory log is being generated. Continue logging until the bottom of the boring is encountered. At this point switch the logging direction switch to the middle position and rotate the speed control fully counterclockwise. Lift the pens off the paper. Now remove the cable slack. The depth reading should correspond closely to the measured depth of the boring. Rotate the paper in each of the recorders until the pens line up on the footage corresponding to that on the depth indicator. Lower the pens. Switch the logging direction switch to the "up" position and rotate the logging speed control until the logging speed reads at or below 10 feet per minute. Maintain the logging speed as close to a constant speed as possible. Continue logging until the sonde reaches the starting position. The pens should be at or near the zero depth position on the chart paper.

Remove the chart paper and record the instrument settings, logging speed, depths, date, well number, operator, job number, and client in pencil on the log.

1.3 Instrument Calibration

Field calibration of the gamma ray sonde is not necessary. The instrument is calibrated during manufacturing and must be periodically checked by the manufacturer.

STANDARD OPERATING PROCEDURE

FOR

OVA

ORGANIC VAPOR ANALYZER

Introduction

The Organic Vapor Analyzer 128 (OVA) is a sensitive instrument designed to measure trace quantities of organic materials in air using a flame ionization detector.

The instrument has broad application since it has a chemically resistant air sampling system and can be readily calibrated to measure almost all organic vapors. It has a single linear scaled readout from 0 ppm to 10 ppm with a x1, x10 and x100 range switch. It is ideal for the determination of many organic air pollutants and for monitoring the air in potentially contaminated areas.

Theory

The OVA 128 instrument utilizes the principle of hydrogen flame ionization for detection and measurement of organic vapors. The instrument measures organic vapor concentrations by producing a response to an unknown sample, which can be related to a gas of known composition to which the instrument has previously been calibrated. During normal survey mode operation, a continuous sample is drawn into the probe and transmitted to the detector chamber by an internal pumping system. The sample stream is metered and passes through particle filters before reaching the detector chamber. Inside the detector chamber, the sample is exposed to a hydrogen flame which ionizes the organic vapors. When most organic vapors burn, they leave positively charged carbon-containing ions. An electric field drives the ions to a collecting electrode. As the positive ions are collected, a current corresponding to the collection rate is generated. This current is measured with a linear electrometer preamplifier which has an output signal proportional to the ionization current. A signal conditioning amplifier is used to amplify the signal from the preamp and to condition it for subsequent meter or external recorder display.

Operation

Start-Up Procedure

- a. Connect the Probe/Readout Assembly to the Sidepack Assembly by attaching the sample line and electronic jack to the Sidepack.
- b. Select the desired sample probe (close area sampler or telescoping probe) and connect the probe handle. before tightening the knurled nut, check that the probe accessory is firmly seated against the flat seals in the probe handle and in the tip of the telescoping probe.

- c. Move the Instr/Batt Switch to the test position. The meter needle should move to a point beyond the white line, indicating that the integral battery has more than four hours of operating life before recharging is necessary.
- d. Move the Instr/Batt Switch to the "ON" position and allow a five-minute warm-up.
- e. Turn the Pump Switch on.
- f. Use the Calibrate Adjust knob to set the meter needle to the level desired for activating the audible alarm. If this alarm level is other than zero, the Calibrate Switch must be set to the appropriate range.
- g. Turn the Volume knob fully clockwise.
- h. Using the Alarm Level Adjust knob, turn the knob until the audible alarm is activated.
- i. Move the Calibrate Switch to x1 and adjust the meter reading to zero using the Calibrate Adjust (zero knob).
- j. Open the hydrogen Tank Valve one or two turns and observe the reading on the Hydrogen Tank Pressure Indicator. (Approximately 150 psi of pressure is required for each hour of operation).
- k. Open the Hydrogen Supply Valve one or two turns and observe the reading on the Hydrogen Supply Pressure Indicator. The reading should be between 8 and 12 psi.
- l. After approximately one minute, depress the Igniter Button until the hydrogen flame lights. The meter needle will travel upscale and begin to read "Total Organic Vapors". Caution: Do not depress igniter for more than six seconds. If flame does not ignite, wait one minute and try again.
- m. The instrument is ready for use.

NOTE: If the ambient background organic vapors are "zeroed out" using the Calibrate Adjust knob, the meter needle may move off-scale in the negative direction when the OVA is moved to a location with lower background. If the OVA is to be used in the 0 to 10 ppm range, it should be "zeroed" in an area with very low background. A charcoal filter can be used to generate the clean background sample.

Shut Down Procedure

The following procedure should be followed for shut down of the equipment:

- a. Close HYDROGEN TANK VALVE
- b. Close HYDROGEN SUPPLY VALVE
- c. Move INSTR Switch to OFF
- d. Wait five seconds and move PUMP Switch to OFF. INSTRUMENT IS NOW IN A SHUT DOWN CONFIGURATION.

Fuel Refilling

NOTE: Use PREPURIFIED or ZERO grade hydrogen (certified total hydrocarbons as methane <0.5 ppm recommended).

- a. The instrument and the charger should be completely shut down during hydrogen tank refilling operations. Refilling should be done in a ventilated area. THERE SHOULD BE NO POTENTIAL IGNITERS OR FLAME IN THE AREA.
- b. If you are making the first filling on the instrument, or if the filling hose has been allowed to fill with air, the filling hose should be purged with hydrogen prior to filling the instrument tank. This purging is not required of subsequent filling.
- c. The filling hose assembly should be left attached to the hydrogen supply tank when possible. Ensure that the FILL/Bleed Valve on the instrument end of the hose is in the OFF position. Connect the hose to the refill connection on the Side Pack Assembly.
- d. Open the hydrogen supply bottle valve slightly. Open the REFILL VALVE and the HYDROGEN TANK VALVE on the instrument panel and place the FILL/BLEED Valve on the filling hose assembly in the FILL position. The pressure in the instrument tank will be indicated on the HYDROGEN TANK PRESSURE Indicator.
- e. After the instrument fuel tank is filled, close the REFILL VALVE on the panel, the FILL/BLEED Valve on the filling hose assembly and the hydrogen supply bottle valve.

- f. The hydrogen trapped in the hose should not be bled off to atmospheric pressure. CAUTION should be used in this operation as described in Step (g.) below, since the hose will contain a significant amount of hydrogen at high pressure.
- g. The hose is bled by turning the FILL/BLEED valve on the filling hose assembly to the BLEED position. After the hose is held down to atmospheric pressure, the FILL/BLEED valve should be turned to the Fill position to allow the hydrogen trapped in the connection fittings to go into the hose assembly. Then, again, turn the FILL/BLEED Valve to the BLEED position and exhaust the trapped hydrogen. Then turn the FILL/BLEED Valve to OFF to keep the hydrogen at one atmosphere in the hose so that at the time of next filling there will be no air trapped in the filling hose.
- h. Close the HYDROGEN TANK VALVE.
- i. With the HYDROGEN TANK VALVE and HYDROGEN SUPPLY VALVE closed, a small amount of HYDROGEN at high pressure will be present in the regulators and plumbing. As a leak check, observe the HYDROGEN TANK PRESSURE Indicator while the remainder of the system is shut down and ensure that the pressure reading does not decrease rapidly (more than 350 psi/h) which would indicate a significant leak in the supply system.

Calibration Using a Single Sample Calibration

Calibration may be accomplished using a single known sample of methane in air in the range of 90 to 100 ppm. This may not provide the accuracy stated under specification but is adequate for field survey work.

- a. Place instrument in normal operation with CALIBRATE Switch set to x10 and GAS SELECT control set to 300.
- b. Use the CALIBRATE ADJUST (zero) knob to adjust the meter reading to zero.
- c. Introduce a methane sample of known concentration (between 90 and 100 ppm, not to exceed 1000 ppm) and adjust trimpot R-32 so the meter reading corresponds to the known sample.
- d. This sets the instrument gain for methane with the panel mounted gain adjustment (GAS SELECT) set at a reference number of 300.
- e. Turn off HYDROGEN SUPPLY VALVE to put out flame.

- f. Leave CALIBRATE Switch on x10 position and use CALIBRATE ADJUST (zero) knob to adjust meter reading to four ppm.
- g. Place CALIBRATE Switch in x1 position and using trimpot R-31, adjust meter reading to four ppm.
- h. Move CALIBRATE Switch to x10 position again. Use CALIBRATE ADJUST (zero) knob to adjust meter to a reading of 40 ppm.
- i. Move CALIBRATE Switch to x100 position and use trimpot R-33 to adjust meter reading to 40 ppm.
- j. Move CALIBRATE ADJUST (zero) knob to adjust meter reading to zero.
- k. Unit is now balanced from range to range, calibrate to methane, and ready to be placed in normal service.

Limitations

The OVA has an inherent limitations in that it can detect only organic molecules. Also, it should not be used at temperatures lower than about 40°F because gases condense in the pump.

It should be noted that due to the compressed hydrogen supply, the instrument cannot be carried on passenger aircraft, and therefore, unless driven to the site, will have to be sent through Federal Express as dangerous goods.

STANDARD OPERATING PROCEDURE

FOR

OVM

OPERATION

1.0 INTRODUCTION

The 580A has seven switches located just below the display. They are labeled:

ON/OFF
MODE/STORE
RESET
LIGHT
+/INC
-/CRSR
SPKR

The ON/OFF switch toggles the lamp and pump power between on and off. The MODE/STORE, RESET, +/INC, -/CRSR and SPKR switches all have various meanings (including none at all) depending upon the mode. The SPKR switch normally is used to toggle the instrument speaker between on and off. Pressing the MODE/STORE switch will cause the 580A to return to the Run mode. Except when the 580A is already in the run mode. In which case it will cause the 580A to enter the log mode.

The light switch is used to run on an incandescent light which is mounted behind the display. This is to allow the use of the 580A in dark areas.

The 580A has several modes. Some of the modes may have sub modes. The modes and sub modes are tabulated below.

Run mode
 Concentration meter normal
 Max hold
Log mode
Parameter mode
 Calibration mode
Access mode
Clock mode
Communication mode

The following sections will describe each mode and how to get to them and through them. It is strongly suggested that this section be carefully read and that the 580A be used along with the manual in order to reinforce the manual.

2.0 RUN AND LOG MODE

2.1 Power for Lamp and Pump

When the 580A is first turned on the display will indicate that the lamp is not lit. Pressing the ON/OFF switch will tell the microprocessor to turn on the lamp and the pump. The microprocessor will send power to the lamp and pump and then "look" to see if the lamp actually lit. If it did not light then the microprocessor will try again. If after six tries the lamp still will not light then the microprocessor will indicate a lamp out condition.

In the event that the microprocessor is unable to light the lamp, check the seating of the lamp. If the problem persists call service.

Once the lamp is lit the display will show the PPM (part per million) on the bottom line. The top line will either be a bar graph or the maximum reading (see Section 2.2).

To turn the lamp and pump off simply press the ON/OFF switch.

2.2 Run Modes

The 580A has two run modes, Max Hold and Concentration meter. The run mode is selected in the Parameters section (see Section 4.3). In the concentration meter mode the top line of the display will be a bar graph. The bar graph is a logarithmic bar graph over the range of 0 to 2000 PPM. The bar graph is intended as a rough visual indication of the current PPM. The bottom line will indicate the exact PPM.

In the Max Hold mode the top line of the display will indicate the maximum reading. The bottom line of the display will indicate the current PPM. Whenever a new maximum is seen the top line will be updated.

2.3 Log Mode

The ability to "log" data is one of the 580A's greatest features. Readings may be stored for later analysis. Each reading will have a date and time as well as a location code associated with it. Up to over 700 readings may be stored. Logged data may even be sent to a printer or computer via an RS232 serial communication port.

The Log mode is entered from the Run mode by pressing the MODE/STORE switch. When this switch is pressed from the Run mode the display will show:

LOG THIS VALUE?

on the top line and either PPM or MAX PPM on the bottom line depending upon which run mode the 580A is current in. By pressing the +/INC switch the display will then show:

LOC. CODE 000001

on the top line (the actual location code may not be 000001). The location code may now be entered. By pressing the RESI and +/INC switches together the number above the cursor may be incremented. By pressing the RESET and -/CRSR switch together the cursor may be moved to the next digit.

Once the desired location code has been entered pressing the MODE/STORE switch will "log" the data point. This means that the reading displayed on the bottom line along with the location code, the current date and the current time will be stored into the 580A's memory. The 580A will then return to the Run mode.

If for any reason logging is not desired, pressing the RESET switch rather than the MODE/STORE switch will cause the value not to be stored. The 580A will then go back to displaying:

LOG THIS VALUE?

Pressing the mode switch will now return the 580A to the Run mode.

2.4 Speaker

While the 580A is in the Run mode the speaker may be turned on. The speaker will generate a "clicking" which will increase in speed as the concentration increases. The purpose of the speaker is to give to operator an audible indication the PPM. The speaker may be turned on or off by pressing the SPKR switch. The speaker rate may also be changed by changing the switches located inside of the side door. Only one of the four speaker rate switches should be on (the down position) at any time.

2.5 Low Battery

The 580A will display a warning when the battery is low. The warning will be a flashing B in the right hand corner the top line of the display when the 580A is in the Run mode. The 580A should be recharged when the low battery warning is activated.

2.6 Overrange

The 580A will display an overrange warning if the concentration goes above 2000 PPM. The top line of the display will show:

OVERRANGE

Once an overrange condition occurs the instrument will "lock out". This means that the overrange warning will continue to be displayed until the instrument is brought to a "clean" area. A clean area is defined to be an area where the concentration of organic vapors is below 20 PPM. The 580 a will continue to indicate PPM on the bottom line during an overrange conditions.

2.7 Alarm

The 580A has an alarm which will sound if the PPM rises above the alarm setting. The alarm setting is entered in the Parameters mode (see Section 4.3). If the speaker is not activated then the alarm will of course not be heard. Once the PPM drops below the alarm setting the alarm will turn off.

3.0 MAIN MENU

By pressing the MODE/STORE switch from the Run mode and then pressing the -/CRSR switch when asked if logging is desired, the 580A will display the main menu.

R/COMM	-/PARAM
+/ACCESS	S/CLOCK

The other four operating modes (Communication, Parameters, Access and Clock) may be entered from the Main menu. The operating mode may always be returned to by pressing the MODE/STORE switch.

4.0 PARAMETERS MODE

All of the 580A operating parameters are entered in the Parameters mode. The 580a is also calibrated from within the Parameters mode. The Parameters mode may be entered by pressing the -/CRSR switch from the main menu.

There are seven different sections in the parameters mode.

1. Run mode selection
2. Average time selection
3. Alarm setting

4. Lamp selection
5. Response factor setting
6. Calibration
7. Free space indication

Pressing the +/INC switch will advance the 580A to the next section. Pressing the -/CRSR will advance the 580A to the previous section. Each section and any of its sub-sections will be described in the following pages. It is important to note that when the 580A is in a sub-section of any of the above sections that the +/INC and -/CRSR switches will have a different meaning. This may seem confusing at first but will become clear after stepping through each section.

4.1 Run Mode Selection

There are two Run modes. Concentration meter normal and Max Hold (see Section 2.2). The top line of the display will show:

CONC. METER

the bottom line will show:

"RESET" TO CHG

the bottom line will alternate every two seconds with:

MAX HOLD

if the 580A is in the Max Hold mode. Pressing the RESET switch will cause the 580A to show:

MAX HOLD
+ = USE/-=NO

if the +/INC switch is pressed then the Max Hold mode will be selected. If the -/CRSR switch is pressed then the Concentration meter normal mode will be selected. In either case the 580A will then return to the previous screen.

4.2 Average Time Selection

The 580A can be configured to display the average PPM every one, five, ten or twenty-five seconds. The display will show:

AVERAGE = 1
"RESET" TO CHG

Pressing the RESET switch will cause the 580A to show:

+/-1 -/5
R/1- S/25

Pressing the +/-INC, -/CRSR, RESET, or SPKR switch will cause the average rate to be 1, 5, 10 or 25 seconds respectively. The 580A will then return to the previous screen.

4.3 Alarm Setting

The 580A will display the current alarm setting on the top line of the display. The setting may be changed by simultaneous pressing the RESET switch with either the +/-INC switch to increment the digit above the cursor or the -/CRSR switch to move the cursor.

4.4 Lamp Selection

The 580A will display:

LAMP

one the top line. The bottom line will alternate every two seconds between:

"RESET" TO CHG

and the currently selected lamp setting.

i.e.

11.8eV

By pressing the RESET switch, the 580A will display:

+/-10eV -/11eV

on the bottom line. Pressing the +/-INC switch will select the 10.0eV lamp. Pressing the -/CRSR switch will select the 11.8eV lamp. In either case the 580A will return to the previous screen.

4.5 Response Factor Setting

The current Response Factor setting will be displayed on the top line of the display. The Response Factor may be changed by simultaneously pressing the RESET switch with either the +/-INC switch to increment the digit above the cursor or the -/CRSR switch to move the cursor.

4.6 Calibration

The 580A will display:

**"RESET" TO
CALIBRATE**

The calibration mode may be entered by pressing the RESET switch. The 580A will display:

**ZERO GAS
RESET WHEN READY**

Once zero gas has been introduced the RESET switch should be pressed. The 580A will then zero the instrument. The 580A will display:

**MODEL 580A
ZEROING**

Once the 580A has been zeroed the 580A will display:

SPANPPM = 0000

The Span gas concentration may now be entered by simultaneously pressing the RESET switch and either the +/-INC switch to increment the digit above the cursor or the -/CRSR switch to move the cursor. Once the span gas concentration has been entered the +/-INC switch should be pressed.

The 580A will then display:

SPAN GAS
RESET WHEN READY

Once the span gas has been introduced the RESET switch should be pressed. The 580A will then calibrate the instrument. The 580A will display:

MODEL 580A
CALIBRATING

Once the 580A has been calibrated the 580A will go back to the beginning and display:

"RESET" TO
CALIBRATE

If during the zeroing or calibrating of the 580A a steady reading was not seen then the 580A will display:

CAL ERROR
RESET WHEN READY

Pressing the RESET switch will return the 580A to zeroing or calibrating (depending of course on which it came from).

4.7 Free Space Indication

This section will give a rough indication of how much room is left for logging data points. The screen will display a bar graph on the top line and the amount of free space on the bottom line. The number indicates the total number of bytes which are available. Each data point take fifteen bytes. Other bytes may also be needed in order to store other important information. This is why only a rough indication of room may be given.

5.0 ACCESS MODE

The Access mode is entered by pressing the +/-INC switch from the main menu. The 580A has four access levels, zero through three. Level zero will only allow the operator to log data points and of course to change access levels (only if the access code is known). Level one will also allow the user to change the use identification number. Level two will allow the user complete access to the Parameters mode, and allow viewing of the date and time. Access level three allows complete access.

The access mode has three sections:

1. Access level
2. User identification number
3. Instrument number

Pressing the +/INC switch will advance the 580A to the next section. Pressing the -/CRSR switch will advance the 580A to the previous section.

5.1 Access Level

The screen will display:

ACCESS LEVEL 3
"RESET" TO CHG

By pressing the RESET switch the 580A will display:

KEY 00003
"RESET" WHEN DONE

Please note that in both screens the 3 indicates the current access level and may not necessarily be a three.

In order to change the access level the +/INC switch may be pressed to increment the digit above the cursor and the -/CRSR switch may be pressed to move the cursor. The desired access level should be entered in the right most digit. Note that only access levels between zero and three are legal. The remaining four digits are the access code. The access code will be 0000 when the instrument is shipped. The access code should then be entered. Once this is done press the RESET switch. The 580A will then return to the previous screen.

If the access code entered was not the proper access code, or if the access level was not a legal access level then the access level will not be changed.

The last and most important point regarding the access level is how to change the access code. The access code is the four rightmost digits of the instrument number. The instrument number is only viewable (and therefore only changeable) while in access level three.

5.2 User Identification Number

The screen will display:

**I.D.#014563977
"RESET" TO CHG**

By pressing the RESET switch the 580A will display:

**I.D.#014563977
"RESET" WHEN DONE**

The user identification number may be changed by pressing the +/INC switch to increment the digit above the cursor and the -/CRSR switch to move the cursor. The user identification number is a nine digit number (just right for fitting a social security number). Once the user identification number has been entered press the RESET switch and the 580A will return to the previous screen.

5.3 Instrument Number

The screen will display:

**INSTR #000000
"RESET" TO CHG**

By pressing the RESET switch the 580A will display:

**INSTR #000000
"RESET" WHEN DONE**

The instrument number may be changed by pressing the +/INC switch to increment the digit above the cursor and the -/CRSR switch to move the cursor. ONce the instrument number has been entered the RESET switch should be pressed. The 580A will then display the previous screen.

When the instrument number is changed it is very important that the last four digits be remembered. These digits are the access code and therefore will need to be known in order to change the access level.

6.0 CLOCK MODE

The Clock mode is entered from the Main menu by pressing the SPKR switch. The screen will display the date and time on the top line. The bottom line will display:

"RESET" TO CHG

By pressing the RESET switch the 580A will display:

"RESET" WHEN DONE

The date and time may be changed by pressing the +/-INC switch to increment the number (or in the case of the month the months abbreviation) above the cursor. The -/CRSR switch will move the cursor. Once the proper month has been entered the RESET switch should be pressed. The 580A will return to the previous screen.

The date and time will be maintained even when the instrument is turned off! It is however advisable that the date and time periodically be checked to ensure that it is correct.

7.0 COMMUNICATION MODE

The Communication mode is entered from the main menu by pressing the RESET switch. The Communications mode has four sections.

1. Communicate with printer or computer
2. Display logged data
3. Reset logged data
4. Set communication parameters

Pressing the -/CRSR switch will advance the 580A to the next section.

7.1 Communicate with Printer or Computer

The 580A is capable of communicating with a computer or outputting logged data to a printer. The 580A will display:

COMMUNICATE?

"+" = YES

if the computer format is selected or it will display:

OUTPUT TO PRINTER

"+" = YES

if the printer format is selected. In either case pressing the +/INC switch will cause the 580A to try to establish communication. Pressing the -/CRSR switch instead will cause the 580A to advance to the next section.

7.2 Display Logged Data

If at least one data point has been logged the 580A will display:

DISP. LOG DATA?

"+" = YES

By pressing the +/INC switch the 580A will display the first data point. The date and time which the data point was logged will be displayed on the top line. the bottom line will alternate between the location code and the PPM. Pressing the +/INC switch will advance to the next logged data point. this will continue until there are no more data points at which time the 580A will display:

NO DATA STORED

The MODE/STORE switch may be pressed to return to the Run mode.

7.3 Reset Logged Data

The logged data can be erased so that more data points may be logged. the screen will display:

RESET LOG DATA?

"+" = YES

Pressing the +/INC switch will erase all of the logged data points. The 580A will then advance to the next section.

7.4 Communications Parameters

The 580A can be configured to communicate with a printer or a computer. The baud rate may also be set for 9600, 4800, 2400, 1200, 900, 600, 300, or 150 baud. The 580A will display the current communication format (computer or printer) on the top line and the

current baud rate on the bottom line. Pressing the RESET switch will cause the 580A to display:

COMPUTER FORMAT

+ = USE - = NO

Pressing the +/-INC switch will select the computer format and the 580A will advance to the baud rate screen (see below). Pressing the -/CRSR switch will cause the 580A to display:

PRINTER FORMAT

+ = USE - = NO

Pressing the +/-INC switch will select the printer format and the 580A will advance to the baud rate screen (see below). Pressing the -/CRSR switch will cause the 580A to display the previous screen.

The baud rate screen will display the currently selected baud rate on the top line. The bottom line will display:

+ = USE - = NO

Pressing the +/-NC switch will cause the displayed baud rate to be selected and the 580A to show the selected format on the top line and the baud rate on the bottom line. Pressing the -/CRSR switch instead will cause the next lowest baud rate to be displayed.

CALIBRATION

1. GENERAL

The Model 580a Organic Vapor Meter is indeed a quantitative instrument and can certainly be used as such. It makes use of the Photoionization Detection System using a lamp with an ionization energy of 10.0eV which is standard in the Model 580A. Almost all organic materials will be ionized at this energy level. There are some organic materials, such as a few of the freons, methane, ethane and propane that are not ionized and thus will not be detected. The ionization potentials for the various organic materials will simply tell whether the material will be detected by the Photoionization Detector. It does not give any clue as to the sensitivity of that detector for that particular material. Certainly, different organic vapors will have different sensitivities. It is important to understand that the MODEL 580A does indeed sense most organic vapors and that its response to these different organic vapors will indeed be different.

In this section of the manual, the aspects of calibrating the Model 580A for various vapors will be discussed. In the following section discussing applications, various ways of using the features of the Model 580A will be explained along with the various methods for calibration of the 580A. There will also be applications of the Model 580A in specific instances where the organic vapors or the mixtures of organic vapors are completely unknown. The 580A can be an extremely useful tool even in areas such as those.

Factory Calibration of the Model 580A

To complete testing and operation in the checkout area, each Model 580A has been calibrated and linearity checked at the factory. The particular gas chosen for this calibration is isobutylene. The Model 580A has good response for isobutylene. Isobutylene standards prepared in air are relatively stable with time, undergoing no serious adsorption or reaction problems.

Methods of Generating Concentrations of Various Materials in Air

This section is not intended to be exhaustive as far as the preparation of gas and vapor standards in air are concerned. Only those methods that have been found most practical for the calibration of the 580A are discussed here. There are basically two types of standards. Static standards in which a known volume of the gas or vapor is mixed with a known volume of air and the concentration of the gas or vapor in air calculated from knowing these volumes. The second method used is what is called a dynamic standard. Dynamic standard preparation involves mixing gases or vapors with air under a flowing condition whereby the flow rate of both gases are known prior to their mixing. The concentration then is calculated from flow rates.

Certainly commercially available standard cylinders of gaseous materials in air offer the most convenient method of calibration. However, these are static standards. Standards prepared in this fashion in air for vapors of various organic liquids often show concentration reduction with time due to adsorption problems. In general, gases when mixed with air will maintain their concentrations with time since adsorption is generally not a problem. However, some gases are sufficiently reactive that chemical reaction of the gas will cause a reduction of it in air. These precautions must be observed when using commercially prepared standards for calibration of the Model 580A. It is for this reason that isobutylene in air was chosen as a reference standard for factory calibration. Static standards can be prepared in a laboratory and in general are reasonable ways of calibrating the Model 580A. However, it is important that these standards be used shortly after their preparation to reduce the significance of any adsorption problems. Static standards prepared for calibration of the Model 580A are best prepared in collapsible plastic bags. This as opposed to a fixed volume container. The sampling rate of the 580A, which is 500 ml/min, requires an appreciable amount of sample. Even one

minute's sampling out of a fixed container will remove 500 mg/min from it. This should not significantly reduce the pressure inside the container. Thus, the collapsible bag provides the best means as opposed to a fixed volume. A 5 gallon polyethylene bag is a convenient size to use of the preparation of static standard.

A tube is inserted into the opened end of the bag and the bag opening then sealed around the tube. The tube should have a cutoff valve or some means of closing the volume of the bag. The volume of air introduced into the bag must be measured. This is most conveniently measured by a wet test meter. However, a source of air flowing through a flow meter can be used if the flow can be held constant, then time is a measure of the volume of the air placed into the bag. All air is expelled from the bag by completely collapsing it prior to connection to the source of air. It can then be connected to a wet test meter or flow meter via a short length of rubber tubing hooked to the plastic cube of the bag. The air flow is started into the bag at a rate of approximately 5 l/min. A total of 10 liters is a convenient volume for a 5 gallon bag. This would mean approximately 2 minutes for filling the bag.

For gaseous samples, the trace organic will be added via a glass hypodermic syringe. The 1 cc Tuberculin syringe is a convenient size. For an isobutylene standard, the 1 cc syringe is flushed with pure isobutylene and then filled to the 1 cc mark. While the air is flowing into the plastic bag, the short piece of rubber tubing is pierced by the needle from the 1 cc syringe and the plunger slowly depressed such that the 1 cc of isobutylene is added to the air flowing into the plastic bag. When 10 liters of air have been added to the plastic bag, the flow is immediately stopped and the valve on the tube or the closing clamp is applied to contain the air and isobutylene within the plastic bag. It is best at this stage of the procedure not to rely solely on the diffusion of isobutylene to form a uniform mixture inside the plastic bag. Slight kneeding of the plastic bag will hasten the mixing of the isobutylene in air. The plastic tube from the bag is then connected to the probe on the Model 580A via a short length of rubber tubing and the valve on the plastic tube immediately opened. The Model 580A withdraws a sample from the bag at the sampling rate of 500 ml/min. Thus, 10 liters of sample in the bag will provide approximately 20 minutes. Certainly the calibration of the 580A can be accomplished in a shorter period of time. The concentration of isobutylene in ppm by volume will be equal to the sample size, which was 1 cc, divided by the volume of the bag in liters, which would be 10 liters, times 1000. In this particular instance, the concentration would be:

$$\frac{1 \text{ cc Isobutylene} \times 1000}{\text{Conc (ppm by Vol)- } 10 \text{ L Air}} = 100 \text{ ppm}$$

For organic materials, which are normally liquids at room temperature, the procedure is essentially the same except that an extremely small liquid sample is injected into the flowing air stream rather than the gas sample. This technique works well only for relatively volatile organic materials. The flowing air stream must vaporize all of the

material or the calculation will be off. If the material is not rapidly volatile in that flowing air stream, the liquid should be injected through the surface of the plastic bag. Immediately after withdrawing the needle, the hole in the plastic bag should be covered with a piece of plastic tape.

Again significant kneeding of the bag will hasten the evaporation of the sample and mixing of the vapor into the air to provide homogeneous samples. The introduction of this sample into the 580A is the same as before. The calculation of the concentration of the vapor in air is a two-step procedure whereby the small volume of liquid injected into the air stream or into the plastic bag is converted to a volume of vapor. This volume of vapor is then used in the same manner as the volume of gas in the case of isobutylene. the following equations apply:

$$\text{Volume Vapor (cc)} = \frac{\text{Liquid Volume (ul)} \times \text{Liquid Density} \times 24.45}{\text{Molecular Weight}}$$

The above equation give the vapor volume at atmospheric pressure (760 torr) and 25 C (77 F).

$$\text{Then:} \quad \frac{\text{Vapor Volume (cc)} \times 1000}{\text{Concentration (ppm by Volume)}} = \text{Air Volume (liters)}$$

The following is a sample calculation for benzene.

$$\text{Liquid Volume} = 2 \text{ ul}$$

$$\text{Benzene Density} = 0.879 \text{ g/cc}$$

$$\text{Molecular Weight Benzene} = 78.1$$

$$\text{Air Volume} = 10 \text{ liters}$$

$$2 \times 0.879 \times 24.45 = 0.55 \text{ cc Benzene Vapor}$$

$$\text{Vapor Volume} = 78.1$$

$$\text{Conc} = \frac{3.55 \times 1000}{10} = 55 \text{ ppm (vol)}$$

The syringe used for the measurement of liquids in this particular instance is a small volume-type such as those manufactured by the Hamilton Company. A convenient size syringe is the 10 microliter volume.

Dymanic standards can be prepared of both gases and vapors by using the techniques of either permeation tubes for gases or diffusion tubes for vapors. These permeation or diffusion devices supply a very small flow of either the gas or vapor. This is mixed with a known flow rate of air providing a flowing stream that has a known amount of either gas or vapor in the air stream. These are probably the most reliable and accurate standards available for low level concentration of gases and vapors in air. However, the techniques require some additional instrumentation in order to implement the use of these devices.

STANDARD OPERATING PROCEDURE

FOR

CG/O₂/H₂S/METER

COMBUSTIBLE GAS/OXYGEN MONITOR/H₂S METER

Introduction

The CG/O₂/H₂S monitor is a continuous duty oxygen monitor, combustible gas and hydrogen sulfide monitor combined in a compact, rugged, easily operated and maintained instrument. It has a 3 1/2 digit liquid crystal display (LCD), an audio indicator (alarm buzzer), solid state circuitry and rechargeable nickel cadmium batter pack in a stainless steel case.

Theory

Combustible gas detection is accomplished by means of a catalytic diffusion type sensor that consists of two wound platinum wire elements covered with porous refractory. One element is active, the other is a reference. The combustible gas concentration as a percent of the LED is shown by the display when the push-button switch in the right side of the case is pressed. An integral audible alarm is provided which will sound if the concentrations of combustible gases exceeds a set point. The alarm operates independently of the display.

Oxygen monitoring is accomplished by means of micro fuel cell that provides a current proportional to the concentration of oxygen in the air. The interaction of electrodes and electrolytes within the fuel cell depends on the presence of oxygen. The LCD constantly displays the concentration of oxygen as a percent of the total atmospheric volume. The alarm sounds if the concentration of oxygen falls below a preset level (19.5%).

Operation

To turn on the instrument, unscrew the knurled collar on the carrying strap mounting post. The calibration cover may not be pulled away from the instrument case top. A pin on the calibration cover disengages from the on/off switch inside the case, and the instrument turns on.

Initially, the display will indicate a very high number. For example, 88.0% oxygen. This is due to the fact that the oxygen sensor puts out extraordinarily high signal when it is first turned on. A new oxygen cell may require as long as 15 minutes before it stabilized in the 21% range.

With the knurled collar unscrewed, the calibration cover may be spun aside to allow access to the adjustment potentiometers inside the instrument. The combustibles zero adjustment is on the left near the strap mounting post. The combustibles span adjustment and the oxygen adjustment are accessed through a common hole on the right.

After calibrating the instrument spin the calibration cover so that its pin is in the access hole for the span and oxygen adjustment. Tighten down the knurled collar. The instrument is now ready for use. The readout will continually display the percentage of oxygen present. Combustible gases are also constantly monitored. The display may be converted from oxygen to combustibles by depressing the recessed switch to the right of the readout on the side of the cover.

Calibration

Oxygen Detector

Loosen the knurled collar on the strap mounting post and swing aside the potentiometer access cover. Allow 15 minutes for the oxygen detector to equilibrate before calibration.

In clean air, adjust the oxygen calibration potentiometer (through the hole labeled "o") slowly turn clockwise so that the oxygen is at the percentage set by the user. Final calibration of the oxygen readout should only be done in free air if the user is sure that the air contains the normal 20.9% oxygen. The readout should then be adjusted to 20.9. If there is any doubt of the oxygen content of the air, calibration gas of a known percentage of oxygen in nitrogen should be used.

Combustibles Detector

Before calibrating the combustibles detector, switch on the instrument and allow the sensor to warm up for 15 minutes. In clean air, switch the instrument display to combustibles. Adjust the zero potentiometer (through the hole labeled "z") to obtain a readout 000.

Use the calibration cup to apply combustible gas of a known concentration to the instrument. The rate of gas flow should be 0.5 (± 0.5) liters per minute. Switch the instrument display to combustibles. Use the span potentiometer (through the hole labeled "s") to set the readout to the percent LEL corresponding to the known gas concentration. Variations in the flow rate will cause inaccurate calibration of the instrument.

Remove the test gas and wait for approximately one minute for the gas to completely disperse. Check that the instrument readout returns to 000. Place the potentiometer access cover in its operating position and tighten the knurled collar.

If the instrument cannot be calibrated, the span potentiometer may be at such a low setting that the instrument cannot respond properly. Turn the span potentiometer approximately 15 turns counter-clockwise, and then repeat the calibration procedure described above. Note that the calibration procedure calls for the adjustment of the zero

potentiometer first. The span potentiometer should not be readjusted until the zero potentiometer is properly set.

Standard Operating Procedure for Field Determination of pH

Ground Water, Surface Water and Leachate Analysis

1.0 Method Summary

- 1.1 This is a determination of the activity of the hydrogen ions by potentiometric measurement.**

2.0 Interferences

- 2.1 Temperature is an important factor. The temperature compensator attached to the instrument automatically corrects the pH value displayed by the meter.**

3.0 Instrumentation

**Beckman pH meter
pH probe
Automatic Temperature Compensator (ATC)**

4.0 Materials and Reagents

**Sample cups
Prepared pH 4 and 10 standards for calibration**

5.0 Calibration

During initial setup and calibration, two standards are run.

Standardizing the Instrument

- 5.1 Depress the CLEAR key to clear the instrument.**
- 5.2 Rinse the electrode with distilled water and immerse in pH 4 buffer. Depress the STANDARD key. When the input from the electrode is stable, the instrument will automatically standardize on the pH value of 4.00 pH buffer. The STD1 symbol and the approximate value of the pH 4.00 buffer will appear in the DISPLAY.**

- 5.3 Rinse the electrode with distilled water and immerse in pH 10 buffer. Depress the STANDARD key again. When the instrument stabilizes, the DISPLAY will include STD1, STD2, temperature, and the approximate value of the pH buffer 10.
- 5.4 The instrument is now ready to make a pH measurement. Rinse the electrode with distilled water and immerse in the sample.
- 5.5 Depress the pH key. Wait until the AUTO symbol flashes and then locks. The DISPLAY will indicate the measured temperature and pH.
- 5.6 This sequence can be repeated for additional pH measurements. Depress the pH key, wait for AUTO READ to lock, and note the pH value.
- 5.7 A +0.05 pH acceptance limit should be used in determining calibration acceptability. If unacceptable, recalibrate as described in 5.1.

6.0 Procedure

- 6.1 Prepare and analyze samples without delay.
- 6.2 Place about 50 mls of sample into a plastic cup and stir with the pH probe.
- 6.3 Allow the pH reading to stabilize. Collect three pH readings from each sample within $\pm .05$ units. Record the pH values on the well or surface water sampling record form. Rinse the probe with distilled water and verify calibration by submersing in a prepared pH standard as described in 5.7.
- 6.4 Proceed to the next sample or location; verify calibration before each measurement.

7.0 Quality Control

- 7.1 Document all calibrations and verification readings, including time and meter readings.
- 7.2 Run duplicate measurements on each batch or every 10th sample.

STANDARD OPERATING PROCEDURE
FOR
CYANIDE MONOTOX

STANDARD OPERATING PROCEDURE

FOR

BECKMAN pH/ METER

APPENDIX F

DETAILED INSTRUCTIONS FOR COMPLETING CLP PAPERWORK AND SHIPPING PROTOCOL

- I. General Superfund Paperwork Requirements**
 - A. Paperwork Requirements for Samples Sent to CLP Labs**
 - B. Paperwork Requirements for Samples Sent to the CRL**
- II. Other Sample Documentation Requirements**
 - A. Chain of Custody Seals**
 - B. Sample Container Tags**
- III. Paperwork Supplies**
- IV. Sample Bottle Ordering**
- V. Specific Instructions for Completing Paperwork**
 - A. Chain of Custody Form**
 - B. Organic and Inorganic Traffic Reports**
 - C. SAS Packing List**
 - D. Central Regional Laboratory Analysis Request Form**
 - E. Central Regional Laboratory Sample Data Report**
 - F. Sample Tag**
 - G. Sample Matrix Log**
 - H. Packaging and Shipping Procedures**

Figures

- 1. Chain-of-Custody Form**
- 2. Organic Traffic Report**
- 3. Organic Traffic Report**
- 4. Inorganic Traffic Report**
- 5. Inorganic Traffic Report**
- 6. SAS Packing List**
- 7. Central Regional Laboratory Analysis Request Form**
- 8. Central Regional Laboratory Sample Data Report**
- 9. Sample Tag**
- 10. Sample Matrix Log**
- 11. Cooler Prepared for Shipment**

I. GENERAL SUPERFUND PAPERWORK REQUIREMENTS

A. Paperwork for Samples Sent to CLP Labs

Paperwork requirements include the Chain of Custody forms, Traffic Report forms, SAS Packing Lists and CRL Sample Data Reports. All of these forms, except for the CRL Sample Data Report are composed of 3-4 different colored non-carbon copies. The destination of each copy is specified on the bottom of each form, however, this needs further explaining.

1. Chain of Custody Form

A Chain of Custody Form must accompany each shipment of samples. The top copy is for the laboratory that will receive the samples. The site name should not be on this copy; the lab should not have this information. The copies must be separated before writing the site name on the CRL copy or the pink copy. the yellow copy should be sent to the CRL. The pink copy can be kept by the sampling entity for their files.

2. Traffic Report Forms

Traffic Reports are used for all RAS organic and inorganic samples. The top copy should be sent to Sample Management Office (SMO) within a day or two of shipping samples. (The site name is on this copy). The pink copy should be sent to the CRL with the Chain of Custody form. The bottom two copies get sent to the lab with the samples. Notice that the site name does not copy onto these last two forms. This is because on these two forms, there is a protective coating on that area of the form on these copies which does not allow the information to copy onto these when filling out the top copy.

It is important that the sampler indicate on the Traffic Reports whether the sample shipment is complete or if there are more samples to be shipped to the label under that Case number. This can be written in any where on the Traffic Report. (Each Traffic Report should have a statement about the status of sample shipment.) Traffic Reports should also be used when routine analyses (RAS) and special analyses (SAS) will be performed at the same laboratory; the additional SAS analyses can be written in.

3. CRL Sample Data Report

This is a single copy form and must be sent to the CRL with the Chain of Custody form and the Traffic Reports. If a copy is required for the sampling entity, one solution is to prepare carbon copies or photocopy it.

4. SAS Packing List Forms

This form is used in place of Traffic Reports for SAS analyses. The top copy should be sent to SMO within a day or two of shipping samples. The second copy, the yellow, should be sent to the CRL with the Chain of Custody, the Traffic Reports (if used) and the CRL Sample Data Report. The bottom two copies get sent to the laboratory with the samples. Note on this form that there is no protective coating on the Site Name area of the form. It is necessary, therefore to not write the site name on the form while these two copies are attached. Like on the chain of custody form, a site code can be used if it is difficult to remember to separate these copies before writing the site name on the top two copies.

5. Paperwork Delivery

Paperwork required by the contract laboratory is sent in a plastic bag taped to the inside top of the cooler with the samples. It is required that the CRL copies of the Traffic Reports, Chain of Custody forms, SAS Packing Lists, and CRL Sample Data Report be received at the CRL, to the attention of the RSCC within 5 days of sample shipment. All paperwork for sampling at a site for the week should be submitted paperclipped together.

Late paperwork reports will be sent to each sampling entity and a copy will be kept on file at the CRL. Late paperwork can delay data review and will affect contractor fee award recommendations. It is the prime contact's responsibility to make sure that all paperwork is filled out accurately and submitted within the time frame mentioned above. The RSCC will arrange training sessions on filling out paperwork for samples if the need arises.

Immediately upon shipment of samples, samplers must call SMO with the following information: Case or SAS number, name of laboratory, date of shipment of samples, airbill (shipment) numbers, carrier, number and matrix of samples, continuations, etc.

SMO must be notified by 3:00 PM, EST, on Friday for samples intended for Saturday delivery/pickup.

B. Paperwork Requirements for Samples Sent to the CRL

1. Chain of Custody Form

This form is required for all Superfund samples. See previous guidance on filling this out.

2. EPA Central Regional Laboratory (CRL) Analysis Request Form

This is analogous to the CLP traffic report forms. This is a single copy form and must be sent with the Chain of Custody in the cooler with the samples.

II. OTHER SAMPLE DOCUMENTATION REQUIREMENTS

A. Chain of Custody Seals

All coolers containing Superfund samples must be sealed with EPA Chain of Custody Seals.

B. Sample Container Tags

Each sample container requires a sample tag.

III. PAPERWORK SUPPLIES

Paperwork for Superfund sampling can be obtained from the RSCC for Region V. Prime contacts can request paperwork by submitting a written request to the attention of the RSCC or this can be done by phone. Prime contacts are responsible for requesting paperwork in a timely manner as their supplies run low.

IV. SAMPLE BOTTLE ORDERING

Sample bottles for Superfund sites are available through the Region V Bottle Coordinator. Superfund bottles will be ordered at least one month in advance of the sampling event. Emergency orders will be filled on an as needed basis.

V. SITE INSTRUCTIONS FOR COMPLETING PAPERWORK

A. CHAIN OF CUSTODY FORM

Illustrated in Figure 1

- 1. Enter first six digits of the CRL log number.**
- 2. Enter site code (do not enter the site name).**
- 3. Obtain full signature of sample team leader.**
- 4. Enter last three digits of the CRL log number.
(eg. SOI, DO2, RO1, etc.).**
- 5. List sampling dates for all samples.**
- 6. List sampling times for all samples.**
- 7. Indicate "grab" "composite" sample with an "X".**
- 8. List station locations.**
- 9. Enter number of containers per sample and container volume (e.g., 2-40 ml).**
- 10. List analyses individually.**
- 11. Construct column heading for traffic report number and list serial numbers for corresponding CRL log numbers.**
- 12. Construct column heading for "tag number" and list tag numbers for each sample container.**
- 13. Obtain signature of sample team leader and carry out chain of custody procedures.**
- 14. State carrier service and airbill number, lab service, and custody seal numbers are written here.**
- 15. Write in the words "CASE" #:" and enter the case number.**

Note: One Chain of Custody should be filled out per shipping container. The purpose of using site code is to prevent the contract laboratory from obtaining the site name. An alternative to using a site code is to separate the copies and write the site name on the copies that get sent to the Region, leaving that field blank on the lab's copy.

This is a three copy form:

The top copy goes to the CLP laboratory with the samples.

The second copy (pink) can be kept by the sampling entity.

The last copy (yellow) goes to the RSCC with other paperwork for the site.

If numbered COC seals are not available from Region V, then the alternate COC seal (a white seal that needs to be signed and dated upon use) should be used. In this case, a note should be made on the COC form indicating that these seals were used instead of the numbered seals.

REGION 8
230 South Dearborn Street
Chicago, Illinois 60604

[illegible]

B. INTRODUCTION AND INSTRUCTIONS FOR USE OF MULTI-SAMPLE ORGANIC AND INORGANIC TRAFFIC REPORTS

Illustrated in Figures 2-5

1. Introduction: Samples and Sample Numbers

Contract Laboratory Program (CLP) multi-sample Traffic Reports (TRs) can document up to twenty samples shipped to one CLP laboratory under one Case Number. The TRs must be used for every shipment of RAS samples to a CLP laboratory.

The CLP's definition of "samples" is based on the RAS analytical program: (1) organic, (2) VOA only (3) inorganic.

The CLP sample is one matrix - water or soil - and consists of all the sample aliquots from a sample station location for analysis in one RAS analytical program. The CLP assigns a unique Sample No. to each such set of aliquots sent to one CLP laboratory. The unique Sample Numbers are printed on the adhesive labels. The samplers must accurately transfer this critical Sample Number to the TR.

Organic Sample Numbers are in the format XX123, and have six labels per strip: four for extractables, and two for VOAs (see attachment). CAUTION: The organic sample labels provide two options for each Sample No. - labels for water samples and labels for soil samples. USE ONLY ONE OF THE TWO OPTIONS. An individual sample will be analyzed as EITHER a water or a soil, but never both. DESTROY THE UNUSED LABELS to prevent duplication of Sample Numbers.

Inorganic Sample Numbers are in the format MXX123 and have seven labels per strip: two for Total Metals, two for Cyanide and three extra (see attachment). Remember that the unique Sample No. must only be used once so DESTROY THE EXTRA LABELS.

Use only the labels provided to the Region in which you are sampling.

Letter Code	
<u>Organics, Inorganic</u>	<u>Region</u>
E, ME	V

REMEMBER:

- TRs must be used for each Case No. with every shipment of samples to each CLP laboratory.
- Organic samples, "VOA Only" samples, and inorganic samples are assigned separate, unique Sample Numbers. Each consists of all the sample aliquots from a sample station location.
- A CLP RAS sample will be analyzed as either a water or a soil sample.
- Prevent accidental duplication of sample Numbers by destroying unused labels.
- Use only the Sample Numbers specific to your Region.

2. Completing the Form - Case Documentation

Enter the Case No. and SAS No. (if applicable) at the top right of the form. Complete the boxes in the header.

Box No. 1:

Type of Activity:

If sampling is under Superfund, circle the code which describes the task of the sampling mission:

PA	Preliminary Assessment
SI	Site Investigation
ESI	Expanded Site Investigation
RIFS	Remedial Investigation Feasibility Study
RD	Remedial Design
RA	Remedial Action
ER	Emergency Response (Removal)
NPLD	National Priorities List Delete
O + M	Operations and Maintenance

If sampling is not under the Superfund program, enter the name of program, e.g., RCRA. Enter the site name, the city, state, and Site Spill ID (provided by Region) in the designated spaces.

Box No. 2:

Regional Information

Enter the Region number, the name of your sampling company, and your name in the designated spaces.

Box No. 3:

Ship To:

Enter the name of the CLP laboratory and its full address in the box. Enter the name of the sample custodian or CLP contact in the box provided.

Enter the beginning and ending sampling dates in the designated spaces.

Enter the date shipped, the carrier code (e.g., F = Federal Express, P = Purolator, etc.) and the airbill number in the appropriate spaces.

3. Completing the Form - Sample Documentation

Carefully transcribe the CLP Sample No. from the printed sample labels on the TR in the space provided.

Complete columns A through E to describe the sample:

Column A, Sample Description:

Enter the appropriate sample description code from Box 6. NOTE: Describe RINSATES or BLANKS as #3 "Leachate" in Column A. Write the word "Rinsate" or "Blank" in Column D, the Special Handling section, or in Column E, the Station Location section. Note: Item #3 "Oil" and Item #7 "Waste" are for RAS PLUS SAS projects only. Do not ship oily samples or waste without making prior arrangements with SMO.

Column B, Concentration:

Organic - If sample is low or medium concentration, enter "L". When shipping RAS plus SAS high concentration samples (previously arranged with SMO), enter "H".

Inorganic - Enter "L" for low concentration, "M" for medium concentration, and "H" for high concentration (under previous RAS plus SAS arrangement). REMINDER: Ship medium and high concentration organic and inorganic samples in metals can.

Column C: RAS Analysis:

Check the analytical fractions requested on each sample.

Column D: Special Handling:

Use this space to specify any special handling requirements. Rinsate or blank samples should be identified as such in this space. When shipping RAS plus SAS samples you may code SAS parameters in the blank space (e.g., A = sulfate, B - Cl, etc.) and enter the codes in this column.

Column E: Station Location:

Enter the station location in the space provided.

IMPORTANT:

SAMPLERS MUST INDICATE ON EACH TRAFFIC REPORT WHETHER SAMPLING IS COMPLETE OR IF MORE SAMPLES WILL BE SHIPPED UNDER THE SAME CASE NUMBER. THIS STATEMENT CAN BE WRITTEN ANYWHERE ON THE FORM THAT DOES NOT OBSCURE NECESSARY INFORMATION, AND CAN BE AS SIMPLE A STATEMENT AS "SHIPMENT COMPLETE FOR THIS CASE" OR "MORE SAMPLES TO COME UNDER THIS CASE."

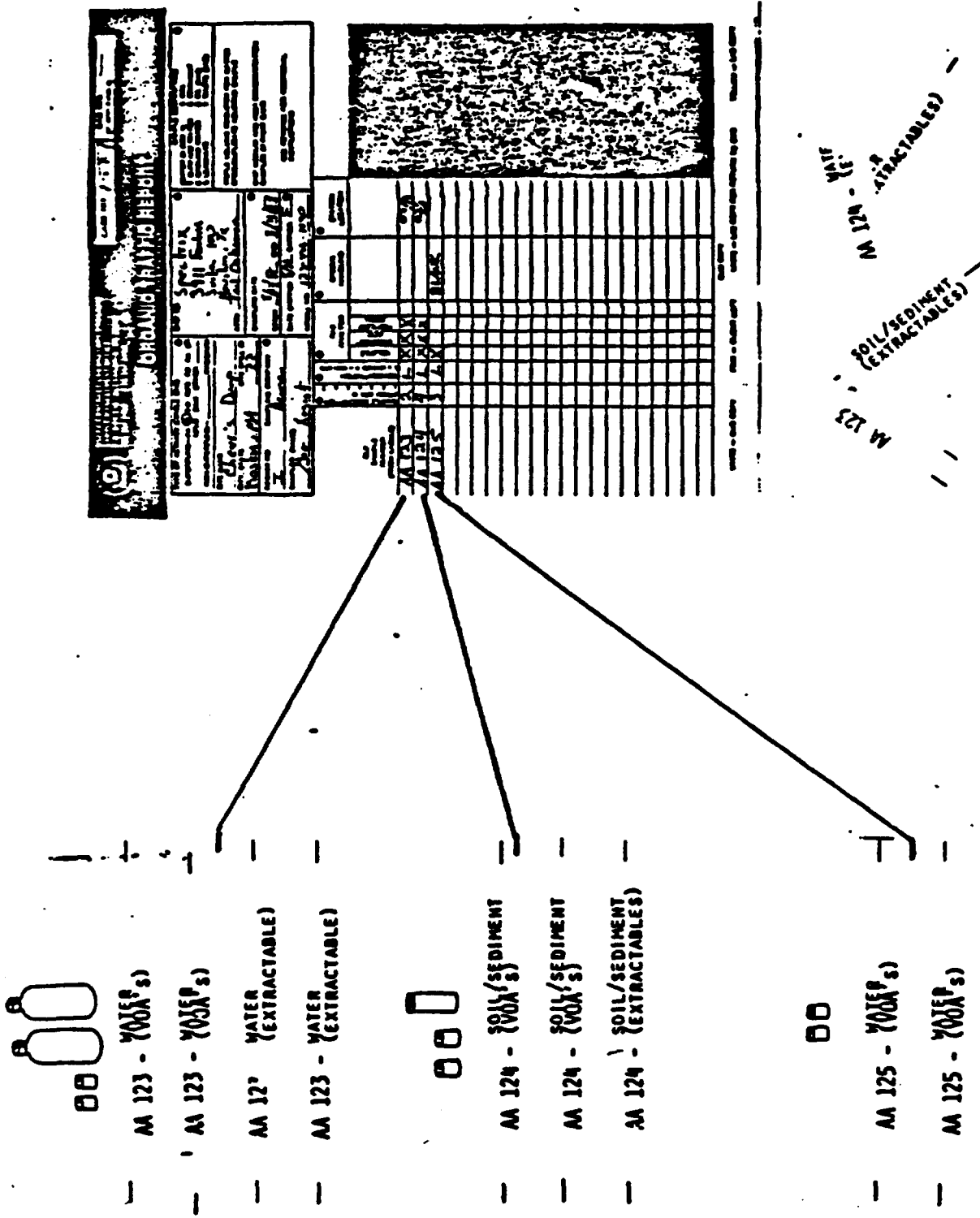


FIGURE 3

TEAR UP THE CORRESPONDING UNUSED SAMPLE LABELS



USEPA CONTRACT LABORATORY PROGRAM

CASE NO: 7588

SAS NO: 3127-A
RE ATTACHED

INORGANIC TRAFFIC REPORT

TYPE OF ACTIVITY (CIRCLE ONE) ① SUPERFUND—PA 88 ESI <input checked="" type="checkbox"/> NO PA 88 WILD OAM OTHER _____ NON-SUPERFUND—_____ PROGRAM _____ SITE NAME: _____ CITY, STATE: <u>Harvard Scraperland</u> <u>Conbridge, MA.</u> SITE SPILL ID: _____ REGION NO: _____ SAMPLING COMPANY: ② <u>I</u> <u>Genetic</u> SAMPLER: (NAME) <u>Rusty Rumpala</u>	SHIP TO: ③ <u>Rocky Mountain Analytic</u> <u>4955 Garwood St.</u> <u>Arvada, CO. 80002</u> ATTN: <u>Kathy Hultman</u> SAMPLING DATE: _____ BEGIN: <u>7/10/77</u> END: <u>7/11/77</u> ④ DATE SHIPPED: <u>7/11</u> CARRIER: <u>F</u> ⑤ AIRBILL NO: <u>123-456-7790</u>	SAMPLE DESCRIPTION (ENTER IN BOX A) 1. SURFACE WATER 4. SOIL 2. GROUND WATER 5. SEDIMENT 3. LEACHATE 6. OIL (RAS) 7. WASTE (RAS) DOUBLE VOLUME REQUIRED FOR MATRIX SP/DUPPLICATE AQUEOUS SAMPLE SHIP MEDIA AND HIGH CONCENTRATION SAMPLES IN PLAST CANS SEE REVERSE FOR ADDITIONAL INSTRUCTIONS
---	--	--

CLP SAMPLE NUMBER (FROM LABELS)	SAMPLE DESCRIPTION (FROM BOX B) 1 2 3 4 5 6 7	CONCENTRATION L - LOW M - MED H - HIGH (BAS)	RAS ANALYSIS						SPECIAL HANDLING	STATION LOCATION	
			TOTAL METALS	CYANIDE	DISSOLVED METALS	HIGH ONLY (BAS)					
						SULFIDE	M	COPPER			ZINC
MAR 123	1	M	X	X						A	01
MAR 124	5	M	X	X						—	02
MAR 125	3	L	X	X						RINSEITE	

A = Max Cyanide

FIGURE 4

WUITE CHAMPION

BOOK - 1 FIRST COPY

Two Copy

WASTE - LAB COPY FOR RETURN TO SMO

YELLOW - LAB COPY

C. SAS PACKING LIST

Illustrated in Figure 6

1. Insert assigned SAS case number.
2. Insert EPA region number (e.g., V).
3. Insert sample team leader's name.
4. Insert sample team leader's office telephone number (do not use field office telephone number).
5. Insert data sample was taken.
6. Indicate date of shipment.
7. Insert site code (do not enter the site name).
8. Insert laboratory name and address.
9. Indicate name of laboratory contact.
10. List SAS sample numbers, which should include SAS number (ie. if the SAS # is 2743, the samples would be numbered as 2743E-01, 2743E-02, etc.)
11. Specify sample matrix, concentration, tag number, and analysis to be performed (e.g., low concentration soil sample for PCB analysis, tag number 5-48246).
12. Leave BLANK - laboratory use only.

NOTE: The site name should not be written on this form while all copies are attached. The CLP laboratory should not have this information. Therefore, either use a site code or separate the copies and only write the site name on the Regional and SMO copies of this form. SAS packing lists are currently being used for high concentration/high hazard analyses and other non-routine work.

THIS IS A FOUR COPY FORM:

The top copy should be sent to SMO within a day or two of shipping samples.

The second (yellow) copy should be sent with other paperwork for a site to the Region V RSCC.

The bottom two copies (pink and gold) get sent to the CLP laboratories with the samples.

U.S. ENVIRONMENTAL PROTECTION AGENCY
 CLP Sample Management Office
 P.O. Box 818 - Alexandria, Virginia 22313
 Phone: 703/557-2490 - FTS/557-2490

SAS Number 1

**SPECIAL ANALYTICAL SERVICE
 PACKING LIST**

Sampling Office: <u>2</u>	Sampling Date(s): <u>5</u>	Ship To: <u>8</u>	For Lab Use Only
Sampling Contact: <u>3</u> (name)	Date Shipped: <u>6</u>		Date Samples Rec'd: _____
<u>4</u> (phone)	Site Name/Code: <u>7</u>	Attn: <u>9</u>	Received By: _____

Sample Numbers	Sample Description I.e., Analysis, Matrix, Concentration	Sample Condition on Receipt at Lab
1. <u>10</u>	<u>11</u>	<u>12</u>
2. _____	_____	_____
3. _____	_____	_____
4. _____	_____	_____
5. _____	FIGURE 6	_____
6. _____	_____	_____
7. _____	_____	_____
8. _____	_____	_____
9. _____	_____	_____
10. _____	_____	_____
11. _____	_____	_____
12. _____	_____	_____
13. _____	_____	_____
14. _____	_____	_____
15. _____	_____	_____
16. _____	_____	_____
17. _____	_____	_____
18. _____	_____	_____
19. _____	_____	_____
20. _____	_____	_____

For Lab Use Only

White - SMO Copy, Yellow - Region Copy, Pink - Lab Copy for return to SMO, Gold - Lab Copy

D. ENVIRONMENTAL PROTECTION AGENCY - Central Regional Laboratory Analysis Request Form.

Illustrated in Figure 7

- 1. Insert sampler name, i.e., WW, Fit, E&E, EDI, or RPM name.**
- 2. Insert sampling date.**
- 3. Insert DU number (Y905 or Y306).**
- 4. Insert site name.**
- 5. Insert priority code (if any).***
- 6. Insert CRL log numbers.**
- 7. Insert sample tag number.**
- 8. Indicate analyses required by placing an "X" in the appropriate column for each sample.**

*** Normal turnaround time for the CRL is 21 days from receipt of samples. Priority 1 analysis requires a 5 day turnaround, and must be requested via a memo from the WMD Director to the ESD Director in advance of sampling. Requests for shorter than the 21 day (and greater than 5 days) turnaround must be addressed to the CRL Director.**

ENVIRONMENTAL PROTECTION AGENCY FOR THE TEAM: METALS, MINERALS-NUTRIENTS

VISION/BRANCH _____

SAMPLE DATE _____

LAB ARRIVAL DATE _____

DUE DATE _____

U NUMBER _____

DATA SET NUMBER _____

STUDY _____

PRIORITY _____

CONTRACTOR _____

CAL LOG NUMBER

SAMPLE DESCRIPTION

TOTAL
METALS
WATER
TOTAL REAP
UNIT

TOTAL
METALS
WATER
AS (breaks)
UNIT

TOTAL
METALS
WATER
Pb (Lead)
UNIT

TOTAL
METALS
WATER
Cd (Antimony)
UNIT

TOTAL
METALS
WATER
Se (Selenium)
UNIT

TOTAL
METALS
WATER
Tr (Thallium)
UNIT

TOTAL
METALS
WATER
Cd (Cadmium)
UNIT

WATER
MERCURY
UNIT

WATER
CHLORIDE
UNIT

FIGURE 7

**E. CENTRAL REGIONAL LABORATORY SAMPLE DATA REPORT
(CRL-SDR)**

Illustrated in Figure 8

- 1. Insert assigned laboratory case number.**
- 2. Insert site name.**
- 3. Insert laboratory names, indicating which lab will receive the organic samples and which lab will receive the inorganic samples.**
- 4. Insert date of shipment.**
- 5. Insert DU code (either Y905 for site inspection or remedial, or Y306 for enforcement, including PRP sites).**
- 6. Insert name of RPM (the RPM will know what the site DU code is).**
- 7. Insert page number and total number of pages.**
- 8. Insert CRL log number, which consists of the fiscal year, EPA assigned contractor code, sample code, round of sampling, sample type designation and sample number.**

eg. 8 8 Z H 2 0 S 0 1
 a b c d e

a = FY (Fiscal Year)

b = Contractor Code (Always ZH for WW Engineering and Science)

**c = Number to be assigned by WW Engineering and Science Paperwork
Coordinator**

d = sample type, could be:

S = sample

D = duplicate

R = field blank

e = sample number ie. 01, 02, 03, etc.

88ZH20S01 - would be a sample.

88ZH20D01 - would be a field duplicate of sample 88ZH20S01.

88ZH20R01 - would be a field blank.

- 9. Insert organic traffic report number.**

10. Insert inorganic traffic report number.
11. Indicate the analyses required (eg. acid-base neutral compounds, volatile organics analysis, etc.) for each sample in the appropriate section (for waters or soils) with an "X".

NOTE: All samples should have a unique number. If the same location will be sampled at a site two weeks in a row, the sample number for the first week could be 88ZH20S01, and for the second week 88ZH21S01. If a sample is collected for filtered and unfiltered metals analyses, a separate ITR should be filled out for each bottle (the filtered and unfiltered). Each one of these samples would then be assigned a unique CRL log number. In order to distinguish between the filtered and unfiltered samples, they can be listed in pairson the CRL-SDR and a column heading indicating "filtered metals" could be created and checked off for the filtered sample.

THIS IS A SINGLE COPY FORM:

This form must be filled out for all Superfund samples which will go to contract labs and must be sent to the Region V RSCC with the other paperwork required for a site.

THIS FORM IS TO BE USED FOR SAMPLES SENT TO CONTRACT ONLY

SUPERFUND CU NUMBER 5 EPA RPM (S.M.S.)/(CES) 6 PAGE 7 OF 7

ACTIVITY NUMBER _____	WATER OR LIQUIDS	SEDIMENTS
-----------------------	------------------	-----------

[illegible]

F. SAMPLE TAG

Illustrated in Figure 9

- 1. Enter the first six digits of the CRL log number.**
- 2. Enter the last three digits of the CRL log number.**
- 3. Enter date of sampling.**
- 4. Enter time of sampling (military time only).**
- 5. Specify "grab" or "composite" sample with an "X".**
- 6. Insert station location.**
- 7. Obtain signature of sample team leader.**
- 8. Indicate presence of preservative with an "X".**
- 9. Specify analytes for analysis with an "X".**
- 10a. Indicate traffic report type and serial number (ITR or OTR and #).**
- 10b. Indicate case number.**
- 11. Leave BLANK (for laboratory use only).**
- 12. Enter any desired analyses not listed on menu provided (e.g., PCB's, ammonia, sulfide, etc.) and mark box with an "X".**

NOTE: Each sample container should have a separate tag. All field blanks should be designated as such on the sample tags, either in the "Remarks" field (10a and 10b) or in the "Station Location" field (6).

Sample Tag

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 5
230 South Dearborn Street
Chicago, Illinois 60604

Front

Project Code (1)

Station No. (2)

Month/Day/Year (3)

Time (4)

Day (5)

Comp. (6)

Station Location (6)

Samples (Signature) (7)

Preservative: Yes ☐ No ☐ (8)

ANALYSES

BOD	Anions
Solids (TSS) (TDS) (SS)	
COD, TOC, Nutrients	
Phenolics	
Mercury	
Metals	
Cyanide	
Oil and Grease	
Organics GC/MS	
Priority Pollutants	
Volatile Organics	
Pesticides	
Mutagenicity	
Bacteriology	

Remarks:

(10a)

(10b)

Tag No. 5- 32261

Lab Sample No. (11)

Back

Each cooler should have 2 CDC seals applied.

U.S. ENVIRONMENTAL PROTECTION AGENCY
REGION V
OFFICIAL SEAL

No. 13400

Chain of Custody Seal

FIGURE 9

G. SAMPLE MATRIX LOG

To assist the team in tracking the samples throughout the investigation, a Sample Matrix Log will be completed as an on-going task during sample collection. The Sample Matrix Log serves two purposes. First, it provides the individual completing the paperwork with an invaluable tool for keeping track of crucial shipping information (dates, airbill numbers, etc). Second, it provides WW Engineering and Science with the information necessary for record keeping within a computer data base. This chart must be maintained daily. The Sample Matrix Log is illustrated in Figure 10.

Completion Requirements

1. Enter the case number.
2. Enter the WW Engineering and Science sample location number.
3. Enter the CRL sample identification number
4. Specify the Sample Matrix using the 2-digit codes listed below:
 - SB - Soil Boring
 - SW - Surface Water
 - PW - Private Well
 - GW - Groundwater (Monitoring Well)
 - SD - Sediment
 - LW - Leachate Waste *water*
 - WA - Lagoon Waste
5. Indicate the concentration (low, medium, or high) by using the letters L, M, or H.
6. Enter the date the sample was taken: month, day, year (no hyphen or slash, e.g.: 051284).
7. Enter the shipping date.
8. Indicate the laboratory to be doing the analysis.
9. Enter the airbill number of the shipment.
10. Enter the custody seal number.

11. Enter the chain-of-custody report number.
12. Enter the organic traffic report number.
13. Enter the inorganic traffic report number.
14. List sample tag numbers corresponding to sample containers shipped under the traffic report number listed in either box 12 or 13.
15. Enter the quality control lot number from the container.
16. Indicate the site name and site number.
17. Enter date matrix completed.
18. Indicate originator.
19. Indicate reviewer.
20. Indicate page number of matrix log.

NOTE: Data recorded on this form must be suitable for computer entry. If portions of samples are to be sent to more than one laboratory for analysis, allow an entire line for each laboratory to accommodate for the additional traffic report, chain-of-custody, and airbill numbers.

[illegible]

H. PACKING AND SHIPPING PROCEDURES

Sample packaging and shipping procedures are based on U.S. EPA specifications as well as Department of Transportation (DOT) regulations (49 CFR). The procedures vary according to sample concentration and matrix and are designed to provide optimum protection of samples and the public.

All samples are to be shipped via Federal Express, Purolator, or Emery as specified in the U.S. EPA Region V Sample Handling Protocol for Hazardous Waste. Shipping containers must be insulated, durable, and watertight. Bagged samples are to be cushioned within the shipping container with vermiculite packing materials (Zonolite) or with bubble pack.

Following shipment, airbill numbers (and other miscellaneous information given in step 18) must be called in to the Sample Management Office.

Step-by-step packing instructions are provided below.

LOW-CONCENTRATION SAMPLES

1. Prepare cooler(s) for shipment
 - Tape drain(s) shut.
 - Affix "This Side Up" labels on all four sides and "Fragile" labels on at least two sides of each cooler.
 - Place mailing label with laboratory address on top of cooler(s).
 - Fill bottom of cooler(s) with about three inches of vermiculite.
 - Place appropriate traffic reports, SAS packing lists, or CRL data sheets and chain-of-custody records with corresponding custody seals on top of each cooler.
2. Arrange decontaminated sample containers in groups by sample number.
3. Mark volume levels on bottles with a grease pencil.
4. Secure appropriate sample tags around caps/lids of containers with string or wire.
5. Secure container caps/lids with strapping tape.

6. Arrange containers in front of assigned coolers.
7. Affix appropriate adhesive labels from assigned traffic report to each container. Protect with clear label protection tape.
8. Seal each container within a separate plastic bag.
9. Arrange containers in coolers so that they do not touch.
10. If ice is required to preserve the samples, cubes should be repackaged in double zip-loc bags and placed on and around the containers (especially on VOA vials).
11. Fill remaining space with vermiculite.
12. Sign chain-of-custody form (or obtain signature) and indicate the time and date it was relinquished to Federal Express, purulator, or emery.
13. Separate copies of forms. Seal proper copies within a large zip-loc bag and tape to inside lid of cooler. Place remaining copies in a large mailing envelope to be sent to the sample documentation coordinatory with a completed transmittal notice.
14. Close lid and latch.
15. Carefully peel custody seals from backings and place intact over lid openings (right front and left back). Cover seals with clean protection tape.
16. Tape cooler shut on both ends, making several complete revolutions with strapping tape (do not cover custody seals). See Figure 11 for an illustration of a cooler ready for shipment.
17. Relinquish to Federal Express. Place airbill receipt inside the mailing envelope and send to the sample documentation coordinator along with the other documentation (Item 13).
18. Telephone the Sample Management Office
Ms. Leslie Braun (subject to change)
Phone Number: (703) 557-2490

Provide the following information:

- Your name
- Project name
- Case number
- Number of samples sent to each lab for analysis
- Airbill numbers/shipper
- Chain-of-Custody numbers
- Traffic report numbers

This must be done immediately following sample shipment.

MEDIUM AND HIGH CONCENTRATION SAMPLES

Medium and high hazard samples shipped by WW Engineering and Science personnel are subject to DOT regulations. Therefore, to comply with the prescribed regulations, all WW personnel must abide by the following procedures.

1. Collect samples in appropriate containers as required by CLP. No preservatives are used for medium and high hazard samples. Assure that the sample container cap is sealed with tape.
2. Attach sample tags to each sample as required by CLP.
3. Place each sample in a ziplock bag in such a way that the sample tag can be read.
4. Place each sealed bag inside a metal can and fill the can with absorbent cushioning material such as vermiculite. The can must be sealed, preferably using clips but tape may also be used.
5. Place the name and address of the laboratory on the can.
6. Place a "Flammable Liquid, n.o.s." or "Flammable Solid, n.o.s." label on the can.
7. Place a "Cargo Aircraft Only" label on the can.
8. Place each can in the shipping container (cooler) which has been lined with two (2) inches of absorbent material.

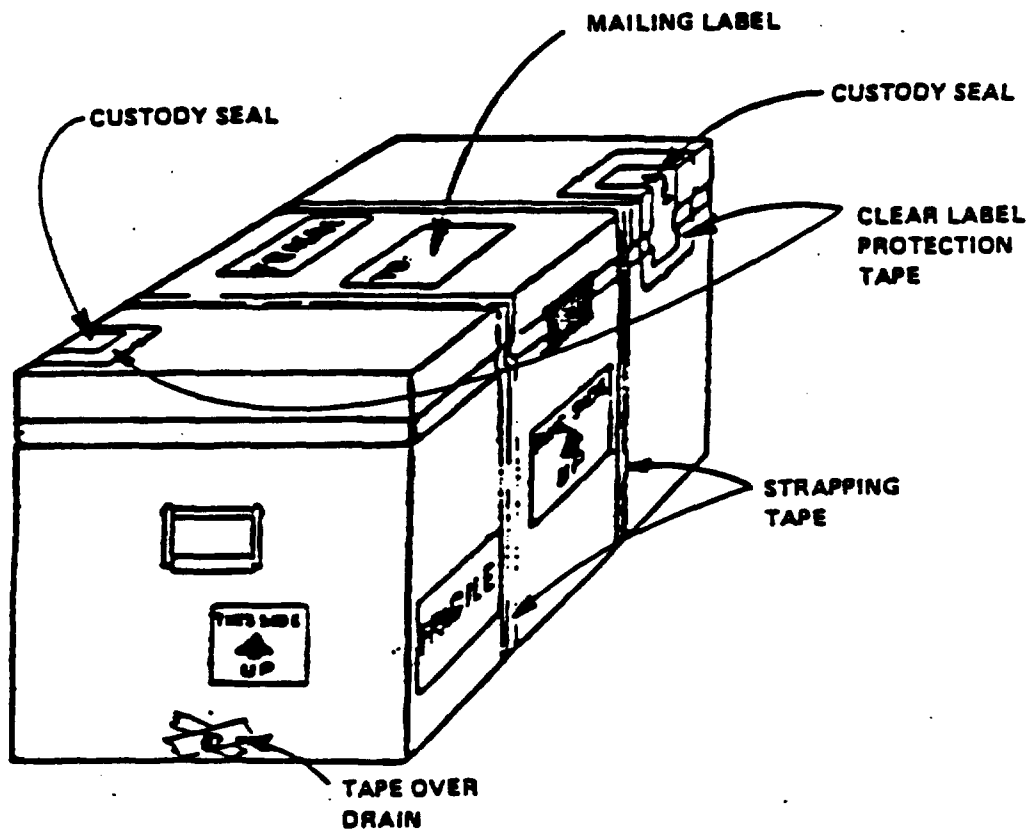
9. Surround each can with absorbent material to prevent sample breakage and provide stability during transport, fill the shipping container with absorbent material.
10. Place all shipping paperwork to accompany the samples, excluding the airbill and Shipper's Declaration of Dangerous Goods in a manila envelope. Secure the envelope in a ziploc bag and place the bag on top of the absorbent material in the cooler.
11. Close and seal the cooler using strapping tape. Place the two custody seals documented on the Custody Record over the shipping container closure.
12. Mark the shipping container with the following information and labels:
 - Shipper's address
 - Laboratory address (consignee)
 - "This End Up," with arrow, label (for liquids only)
 - "Cargo Only Aircraft" label
 - "Inside Containers Comply with Prescribed Regulations" label
 - "Flammable Liquid" or "Flammable Solid" label
 - Additional hand-written label indicating DOT proper shipping name, e.g., "Flammable Liquid, n.o.s. UN1993, " or "Flammable Solid, n.o.s. UN1325"

(This is required only if the "Flammable Liquid" or "Flammable Solid" labels do not exhibit the applicable DOT proper shipping name.)

These labels need only be placed on one face of a cooler. Packages having a volume greater than 64 ft³ (4'x4'x4') require labeling on two sides or ends.

13. To ship packaged samples, the samplers need only to fill out an air bill and for medium and high hazard samples, a Declaration of Dangerous Goods.
14. Same as step #18 for low concentration samples.

FIGURE 11



APPENDIX G
SAMPLE CUSTODY PROCEDURES

APPENDIX G

SAMPLE CUSTODY PROCEDURES

INTRODUCTION

It is U.S. EPA and Region V policy to follow the U.S. EPA Region V sample custody or chain-of-custody protocols as described in "NEIC Policies and Procedures." EPA-330/9-78-001-R, revised June 1986. This custody is in three parts: sample collection, laboratory, and final evidence files. Final evidence files, including all originals of laboratory reports and purge files, are maintained under document control in a secure area.

A sample or evidence file is under your custody if the documents:

- Are in your possession;
- Are in your view, after being in your possession;
- Where in your possession and you placed them in a secured location; or
- Are in a designated secure area.

FIELD SPECIFIC CUSTODY PROCEDURES

The sample packaging and shipment procedures summarized below will insure that the samples will arrive at the laboratory with the chain-of-custody intact.

Field procedures are as follows:

- A. The field sampler is personally responsible for the care and custody of the samples until they are transferred or properly dispatched. As few people as possible should handle the samples.
- B. All bottles will be tagged with sample numbers and locations. The Sample Management Office (SMO) number and stickers will be affixed.
- C. Sample tags are to be completed for each sample using waterproof ink unless prohibited by weather conditions. For example, a logbook notation would explain that a pencil was used to fill out the sample tag because the ballpoint would not function in freezing weather.

- D. The contractor's site manager must review all field activities to determine whether proper custody procedures were followed during the field work and decide if additional samples are required. He or she should notify the U.S. EPA Remedial Project Manager of a breach or irregularity in chain-of-custody procedures.

Transfer of custody and shipment procedures are as follows:

- A. Samples are accompanied by a properly completed chain-of-custody form. The sample numbers and locations will be listed on the chain-of-custody form. When transferring the possession of samples, the individuals relinquishing and receiving will sign, date, and note the time on the record. This record documents transfer of custody of samples from the sampler to another person, to a mobile laboratory, to the permanent laboratory, or to/from a secure storage area.
- B. Samples will be properly packaged for shipment and dispatched to the appropriate laboratory for analysis, with a separate signed custody record enclosed in each sample box or cooler. Shipping containers will be locked and secured with strapping tape and EPA custody seals for shipment to the laboratory. The preferred procedure includes use of a custody seal attached to the front right and back left of the cooler. The custody seals are covered with clear plastic tape. The cooler is strapped shut with strapping tape in at least two locations.
- C. Whenever samples are split with a source or government agency, a separate Sample Receipt is prepared for those samples and marked to indicate with whom the samples are being split. The person relinquishing the samples to the facility or agency should request the representative's signature acknowledging sample receipt. If the representative is unavailable or refuses, this is noted in the "received by" space.
- D. All shipments will be accompanied by the Chain of Custody Record identifying the contents. The original record will accompany the shipment, and the pink and yellow copies will be retained by the sampler for return to the sampling office.
- E. If the samples are sent by common carrier, a bill of lading should be used. Receipts of bills of lading will be retained as part of the permanent documentation. If sent by mail, the package will be registered with return receipt requested. Commercial carriers are not required to sign off on the custody form as long as the custody forms are sealed inside the sample cooler and the custody seals remain intact.

LABORATORY CUSTODY PROCEDURES

A. CONTRACT LABORATORY

The chain-of-custody procedures for Contract Laboratory Program (CLP) are described in Appendix A. This same custody procedure applies to SAS's.

B. CENTRAL REGIONAL LABORATORY

The Central Regional Laboratory has its own regional custody scheme for Drinking Water Specific Samples. There are four possible ways in which the CRL may be involved in chain-of-custody sample tracking:

1. Samples are delivered to the CRL for in-house analysis.
2. Samples are delivered to the CRL. Some are sent out to a contractor and some remain at the CRL, or the samples are sent to several contract laboratories.
3. Samples are delivered to the CRL and the entire shipment is sent to one contract laboratory.
4. Samples are shipped directly from the field to a contract laboratory without ever being delivered to the CRL.

The internal CRL Custody Protocol has been revised so that it addresses all four of these situations and also meets all National EPA custody requirements. Moreover, the revised protocol requires only one new internal document--the Custody Logbook. This logbook replaces the existing Shipping and Receiving Log. The new procedures are applied to the four custody situations as follows;

A. In-House Analysis

Samples are shipped or delivered to the CRL under chain of custody. The CRL Sample Custodian signs the chain of Custody Record in the "Received by" space. The Sample Custodian also signs in the "Received for Laboratory by" space. This document is then complete. It is filed in the folder for the given data set.

The Sample Custodian then enters the following sample information into the Custody Logbook.

- 1, 2, 3 Self-explanatory.
- 4 "Matrix" refers to a brief sample description, such as "water," "oil," "mud," etc. Parameter is self-explanatory.
- 5 Self-explanatory.
- 6, 7, 8 The Sample Custodian initials the date (month/day/year) and the time when samples were received. Time is expressed using a 24-hour clock, so that 1:30 P.M. is recorded as 13.30.
- 9 Each shelf in all custody areas should be numbered, so that the storage location can be identified by the shelf number. This number is entered in column 9.

When an analyst checks out a sample, columns 10 thru 13 are completed.

- 10 The Sample Custodian initials the correct column.
- 11 The analyst initials the correct column.
- 12, 13 The Sample Custodian enters the date and time.

When a sample is transferred from one analyst to another within the CRL, both analysts initial the back of the custody tag. They also enter the date and time.

e.g.: AJ to DM, 9/12/82, 15:30

(It is not necessary to return the sample to the person who originally checked it out of custody.)

When the analyses are completed, the analyst returns the sample to the Sample Custodian. they both fill in columns 14 thru 18.

14, 15, 16, 17, Self-Explanatory.

- 18 The Sample Custodian stores the sample in a custody area. The location is entered in column 18. This is probably not the same as the original location listed in column 9.

When samples are discarded, columns 19 and 20 are filled in. The tags are removed from the sample bottles and are filed in the folder for that data set. TAGS ARE NEVER DISCARDED.

Any appropriate information, including initials, is entered in column 21.

e.g., : "Sample was broken. 10/1/82, AJ"
 "Sample was used up. 10/1/82, AJ"
 "Insufficient sample. 10.1.82, AJ"

Even if a sample is destroyed, the tag must be returned to the custody folder. an explanation should be written on the tag and in the Custody Logbook.

B. Sample Shipments With Several Destinations

Samples are shipped to the CRL under chain of custody. The CRL Sample Custodian receives the shipment as described in Section A. The custodian opens the sealed container, logs in all of the samples, and then repacks those samples which will be sent to a contract laboratory. The Custodian fills out new custody forms and includes them with the shipment as described in the Environmental Services Division (ESD) or National Contract Laboratory Protocols.

The Sample Custodian logs all of the samples into the Custody Logbook. The procedure is the same as described in Section A, with the following exceptions.

- | | |
|------------|---|
| 9 | No entry here. |
| 10 | The Sample Custodian initials here. |
| 11 | The Sample Custodian enters the name of the laboratory to which the samples were shipped. |
| 14 thru 20 | These columns are used only if the contract laboratory returns the samples. |
| 21 | The Sample Custodian enters the shipper and the airbill number. |
- e.g.,: "Emery, #9011625"

C. Entire Sample Shipment Sent to One Destination

Samples are shipped to the CRL under chain of custody. The CRL Sample Custodian receives the samples. The Custodian signs the chain of custody record in the "Received by" space. The Custodian logs in the samples and then packs them for shipment and includes original the chain of custody record with the samples. The custodian does not sign the "Received for Laboratory by" space.

The Sample Custodian logs all of the samples into the Custody Logbook as described in Section B.

D. Samples Shipped From the Field to Contract Laboratories

When samples are shipped directly from the field to a contract laboratory, no one at the CRL signs the chain of custody Record.

The sampling team submits a report to the CRL describing their sampling activities. The Sample Custodian enters that information into the Custody Logbook as follows:

- | | |
|------------|--|
| 1 thru 4 | Self-explanatory. |
| 5 | Tag numbers may not be available in the field |
| 6 thru 9 | Not applicable. |
| 10 | The Sample Custodian enters "field". |
| 11 | The Sample Custodian enters the name of the laboratory to which the samples were sent. |
| 12, 13 | Shipping date and time are entered, if available. |
| 14 thru 20 | These columns are used only if the samples are sent to the CRL by the contract laboratory. |
| 21 | Shipper, airbill number, and any other comments are entered here. |

FINAL EVIDENCE FILES CUSTODY PROCEDURES

The purge files from the Central Region Laboratory (CRL) and Contract Laboratory Program (CLP) are maintained by Region V CRL Laboratory Support Team, Data Coordinator. The purge files include the chain-of-custody sheets, sample tags and raw data records.

The contractor maintains the RI files along with all relevant records, reports, logs, field notebooks, pictures, subcontractor reports and CPMS data reviews in a secured, limited access area and under custody of the contractor's site manager.

ATTACHMENT 1

PREVIOUS DATA

LAGOON SAMPLING CONDUCTED IN 1976

(No sample location map available)

Results on Laboratory Analysis of Samples Collected

@Skinner Landfill, Union Twp., Butler County

Date of Collection: May 11, 1976

Identification of samples (ODH lab number)

#13750-Liquid in pit (black color)
#13751-Liquid in pit (orange color)
#13752-Barrel recovered from pit
#13753-Barrel recovered from pit
#13754-Barrel recovered from pit

Constituent	#13750	#13751	#13752	#13753	#13754
(All results in mg/l(ppm))					
Cyanide	6.76	7.5	0.36	5.4	761
Cadmium	755	180	2.0	5.6	50
Chromium(total)	160	65	4.0	350	126
Lead(total)	1050	285	—	1370	554
Mercury(total)	0.047	0.0135	0.006	0.0]	0.075
Zinc	480	165	20.0	420	325
Copper	185	129	2.1	269	1840
Phenol	27.3	24	12.8	.8.8	11.2

U.S.EPA (Cincinnati lab)

	<u>#13750</u>	<u>#13751</u>
Cyanide	9.1 mg/l	7.7 mg/l

Qualitative determination by gas chromatography-Mass Spectrophotometry process of the constituents in the liquid from Skinner landfill (U.S.EPA Lab-Cincinnati)

Comment: major portion of "ooze" is composed of pesticide intermediat. Compounds: compounds from which pesticides are formulated, and are in their own right toxic.

Trichloropropane
Dichlorobenzene
1, 3 Hexachlorobutadiene (Aldrin Component)
Naphthalene (A major Component)
Hexachlorocyclopentadiene
Methyl Naphthalene (Two Isomers)
Iso-Butyl Benzolate
HexachloroNor-Bornadine (Endrin Intermediate)
Octachloro-cyclo-pentene (The major component, chlordane intermediate)
Heptachlor-nor-borene (Major component-possibly heptachlor intermediate)
Hexachlorobenzene (Major Component)
Chlordene (Chlordane Derivative?)
Methyl Benzyl Phenone
Octachlor penta fulvalene

Table 2-2
QUANTITATIVE RESULTS OF LABORATORY ANALYSIS
PIT COKE AND BARREL LIQUID
SKINNER LANDFILL

Collection Date: May 11, 1976

Constituent (All results in mg/l)	SAMPLE NUMBER				
	<u>013750</u>	<u>013751</u>	<u>013752</u>	<u>013753</u>	<u>013754</u>
Cyanide	6.76	7.5	0.36	5.4	761
Cadmium	755	180	2.0	5.6	50
Chromium (total)	160	65	4.0	350	126
Lead (total)	1,050	285	--	1,370	554
Mercury (total)	0.047	0.0135	0.006	0.01	0.075
Zinc	480	165	20.0	420	325
Copper	185	129	2.1	269	1,840
Phenol	27.3	24	12.8	8.8	11.2

The above samples were tested at the U.S. EPA Cincinnati Lab.

	<u>013750</u>	<u>013751</u>
Cyanide	9.1	7.7

The sample above was tested at the ODH Lab.

Identification of samples

- 013750 - Liquid in pit (black color)
- 013751 - Liquid in pit (orange color)
- 013752 - Barrel recovered from pit
- 013753 - Barrel recovered from pit
- 013754 - Barrel recovered from pit

GLI420/7



RECEIVED
UNITED STATES ENVIRONMENTAL PROTECTION AGENCY IN 7 1976
CINCINNATI, OHIO 45268

Environmental Protection Agency

ENVIRONMENTAL MONITORING AND
SUPPORT LABORATORY - CINCINNATI

June 4, 1976

Mr. John E. Richards
Ohio Environmental Protection Agency
Post Office Box 1049
Columbus, Ohio 43216

Dear Mr. Richards:

As requested by telephone on May 19, 1976, we have analyzed the samples delivered to us by Mr. Ken Harsh on May 20. The results of our examinations to this date are:

Sample Identification

#76-18-#1 Pit Trench

Analytical Result

Total cyanide - 9.1 mg/kg (wet weight)

Organic compounds found and identified:

trichloropropane
dichlorobenzene
1,3-hexachlorobutadiene
naphthalene - a major component
hexachlorocyclopentadiene
methyl naphthalene (2 isomers)
isobutyl benzoate
hexachloronorbornadiene
octachlorocyclopentene - the major component
heptachloronorbornene - a major component
hexachlorobenzene - a major component
chlordane - a major component
methyl benzophenone
octachloropentafulvalene

#76-19-#2 Pit Trench

Total cyanide = 7.7 mg/kg

Organic compounds found and identified:

trichloropropane
dichlorobenzene
1,3-hexachlorobutadiene

naphthalene - a major component
hexachlorocyclopentadiene
methyl naphthalene (2 isomers)
isobutyl benzoate
hexachloronorbornadiene
octachlorocyclopentene - the major component
heptachloronorbornene - a major component
hexachlorobenzene - a major component
chlordane - a major component
methyl benzophenone
octachloropentafulvalene
benzoic acid

The samples are being held under Chain of Custody procedures for further analyses and submission as evidence if required.

Sincerely yours,



Dwight G. Ballinger
Director

Environmental Monitoring and Support Laboratory - Cincinnati

cc: Dr. Edward Glod, Ohio EPA

TAT SAMPLING CONDUCTED IN 1986

(No sample location map available)



River Center, 111 North Canal Street, 8th Floor, Suite 855,
Chicago, IL 60606 • (312) 993-1067

TECHNICAL ASSISTANCE TEAM FOR EMERGENCY RESPONSE REMOVAL AND PREVENTION
EPA CONTRACT 68-01-7367

Mr. Steven J. Faryan
Deputy Project Officer
Emergency Response Section
Western Response Unit
U.S. Environmental Protection Agency
11th Floor
230 South Dearborn Street
Chicago, Illinois 60604

July 20, 1988

TAT-05-G2-00434

Reference: Skinner Landfill, Butler County, Ohio
TDD# 5-8702-07

Dear Mr. Faryan:

On January 28, 1986, the U.S. Environmental Protection Agency (U.S. EPA) tasked the Technical Assistance Team (TAT) to conduct a site assessment of the Skinner Landfill in Union Township, Butler County, Ohio. The enclosed site assessment outlines the background of the site, and describes it as observed in January 1986.

As the site is on the National Priorities List and currently being addressed by the U.S. EPA Hazardous Waste Division, Remedial Section, no action by the Emergency Response Section is recommended. However, based on the existing conditions at the site, the following recommendations are presented for referral to the Remedial Section:

- Establishing a ground water monitoring program for wells in and around the landfill.
- Removing and disposing of contaminated soil near Skinner Creek.
- Staging drums from the northeast side of the landfill for sampling, overpacking, and disposal.

Roy F. Weston, Inc.

SPILL PREVENTION & EMERGENCY RESPONSE DIVISION

In Association with ICF Technology Inc., C.C. Johnson & Associates, Inc., Resource Applications, Inc., Geo/Resource Consultants, Inc., and Environmental Toxicology International, Inc.

WESTON-SPER

Mr. Steven J. Faryan

-2-

July 20, 1988

Should you have any questions or require additional information,
please feel free to contact us.

Very truly yours,

ROY F. WESTON, INC.

Sally Matz

F02 Scott D. Springer
Technical Assistance Team
Leader, Region V

RM/dd
Enclosure

SITE ASSESSMENT

FOR THE

**SKINNER LANDFILL
UNION TOWNSHIP
BUTLER COUNTY, OHIO**

Prepared For:

**U.S. Environmental Protection Agency
Region V
230 South Dearborn Street
Chicago, Illinois**

CONTRACT NO. 68-01-7367

TDD# 5-8702-07

TAT-05-G2-00434

Prepared By:

**WESTON-SPER
Technical Assistance Team
Region V**

July 1988

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1.0 SITE DESCRIPTION

The property utilized by Operating Industries Inc., commonly known as Skinner Landfill, is a demolition debris landfill. Past practices of the landfill involved acceptance of pesticide waste, chemical waste, liquid industrial waste and, allegedly, military chemical ordinance. The landfill is located in Butler County, Ohio, approximately one-half mile northeast of the Town of West Chester, and approximately one-half mile south of the interchange between Interstate 75 and Cincinnati-Dayton Road in Union Township, Ohio, Range 3, Township 2, Section 22 (Figure 1). The Skinner property comprises approximately 78 acres of hilly terrain. The property is bordered on the north and east by wooded land, and on the south by both wooded and agricultural land. To the west is Cincinnati-Dayton Road with an elementary school located across from the Skinner property. The U.S. Environmental Protection Agency (U.S. EPA) Remedial Investigation Feasibility Study (RI/FS) report of the Skinner Landfill states:

"The site is situated in a highly dissected area that slopes from a till-mantled, bedrock upland at elevations of 850 to 900 feet (M.S.L.) to a broad, flat-bottomed valley, which is occupied by Mill Creek, at elevations of 600 to 650 feet. Elevations within the Skinner property range from 650 to 750 feet. The property is traversed by two intermittent streams, one of which, East Fork, flows approximately west to east through the southern part of the site. The other stream, known as Skinner Creek, flows southwesterly, parallel to and about 600 feet east of Cincinnati-Dayton Road. In the angle between the two streams is an upland, having two en-echelon, elongated hills, which are also oriented roughly parallel to Cincinnati-Dayton Road. Several ponds are present on the western flank of the western hill, which shows evidence of sand and gravel extraction.

In general, the site is underlain by relatively thin glacial drift (less than 35 feet) over interbedded shales and limestones of Ordovician age. Based on water well logs and boring logs from the limited on-site investigations, the soils are mixtures of sand, silt and clay in varying proportions. The soil stratigraphy is not well-defined. There appears to be a narrow buried valley that branches off from the Mill Creek buried valley towards West Chester. Drift thicknesses of up to 100 feet were found in West Chester, where a substantial layer of sand and gravel contain an aquifer which serves as a water supply for many residences. This buried valley may extend into the Skinner property at its southeastern corner in the vicinity of the

confluence of the two streams. Preliminary hydrogeologic evaluations by St. John (1981) and Hosler (1976) concluded that ground water flow in the vicinity of the site was most likely in a southwesterly direction, toward the buried valley. However, the depth and configuration of the water table are not well-defined."

2.0 SITE BACKGROUND

The Skinner property first became involved in landfilling in 1934. John R. Kennedy, sanitarian for the Butler County Health Department, states in a 1959 letter that the landfill was used for disposal of general trash from a paper plant, other materials used in the paper making process, and scrap metal from various sources. This letter was written in response to a complaint about late night burning and irritating smoke coming from the Skinner property.

On April 2, 1963, Operating Industries, Inc., requested permission from the Butler County Board of Health (BCBH) to conduct a sanitary landfill operation on the Skinner property in Union Township. The principals of Operating Industries, Inc., included Albert Skinner, Skinner Sand and Gravel Company, and George Solomon of Cincinnati, Ohio. The BCBH approved the use of the site as a sanitary landfill.

The Dalewood Homeowners Association (DHA) opposed the landfill, and subsequently stated their case to the BCBH. On June 25, 1963, the DHA wrote the BCBH, which stated that Skinner Landfill was accepting "liquid cyanide waste" from the Sharonville Ford Motor Company Plant. The DHA further alleged that chemical wastes from Andrew Jurgens Company, Dow Chemical Company, Globe Valve Company, and Cincinnati Chemical Company were being disposed of in Skinner Landfill. In a letter dated June 23, 1964, the Ford Motor Company confirmed that materials containing cyanide were disposed in the Skinner Landfill. No actions were taken regarding these complaints, and the landfill continued operations.

The Southwestern Ohio Air Pollution Control (SOAPC) received a complaint from a citizen on April 19, 1976, concerning heavy smoke and odors emanating from the Skinner Landfill during the period of April 8, 1976, to April 19, 1976. The citizen also reported experiencing eye irritation on April 16, 1976. This same citizen reported seeing two tank trucks enter and leave the landfill. SOAPC inspector Hugh Davis investigated the complaint and reported that the cause of the latest observed fire (April 18, 1976) was the burning of old tires and scrap lumber at the facility. He stated in his report that he could not discern any chemical odor. One fireman reported that they feared the fire would reach a nearby lagoon containing a black, oily liquid. The

surface area of the lagoon was estimated to be approximately 35 feet x 40 feet.

On April 21, 1976, the Ohio Environmental Protection Agency (OEPA) was asked to investigate the latest suspicion of whether waste from the Chem-Dyne Corporation Industrial Waste Storage Plant was being delivered to the Skinner Landfill. The Chem-Dyne Corporation denied that any of their waste was disposed of at the Skinner Landfill site.

After access had been denied on April 22, representatives of OEPA, SOAPC, BCHD, and Butler County Sheriff's Deputies entered the Skinner Landfill on April 26, 1976, with a search warrant. The area of the lagoon noted during the April 18, 1976 fire had been recently graded. This grading allegedly began the afternoon of April 22, 1976, after access was denied. Over one hundred 55-gallon drums marked "Chemical Waste" were also observed during the April 26 inspection.

The OEPA received reports on May 3, 1976, that the Skinners had been trucking unknown materials off their property late at night. The trucks left the landfill with their lights off, and consequently, were not readily identifiable.

On May 4, 1976, representatives of OEPA and the Butler County Sheriff's Department returned to the Skinner Landfill site with a search warrant to conduct further investigations. The inspector found the road leading to the regarded lagoon area blocked by a bulldozer, that the Skinners claimed was inoperable. When the Skinners were told that the OEPA would return with the equipment to move the bulldozer they stated that the following materials were buried at the landfill: nerve gas; mustard gas; incendiary bombs; phosphorous; Flame Throwers; cyanide ash; and explosive devices.

At this time the OEPA withdrew from the site, and inquiries were made into the Skinner's allegations. Sources confirmed only that that cyanide ash, phosphorous, and one or two flame throwers with canisters had been disposed of by the Skinners. No confirmation was available of the other materials claimed to be disposed of on the site. Due to the possible involvement of weaponry, the Pentagon was contacted and a specialized unit was secured to aid in the site investigation.

At a meeting on May 10, 1976, between the Butler County Sheriff, U.S. EPA, and the U.S. Army Special Unit, the Sheriff stated that the Skinners' had been working all Saturday night, Sunday and Sunday night moving earth. Representatives of the OEPA, U.S. Army Special Unit, and Butler County Sheriff's Department entered the Skinner Landfill on May 11, 1976, and proceeded to the lagoon area that had been pinpointed on aerial photographs. As

excavation of the lagoon area was undertaken, a chemical odor became stronger, and individuals in the general area reported experiencing burning eyes and general discomfort. At a depth of 10 feet, the soil removed became black, slimy and moist. At 15 feet, thick black liquid began flowing into the excavated trench. Between 15 to 20 feet, a layer of 55-gallon drums was discovered, as well as red and green material resembling paint. Seven samples were collected from the excavated site and drums. Consultants from Chem-Dyne had stated earlier that there might have been a clay and/or vinyl liner in the lagoon area. No liner was encountered during the excavation.

Analysis of the May 11, 1976, OEPA sampling of pit ooze and drum liquid indicated the presence of several pesticide intermediate compounds as well as cyanide, cadmium, chromium, lead, mercury, zinc, copper and phenol. Despite these findings, the landfill continued operations.

On July 22, 1977, J. Zorn, of Rayan Engineering, took aerial slides of the Skinner Landfill and reported open burning in the disposal site area. The OEPA reinvestigated the Skinner Landfill on July 25, 1977, and made the following observations: demolition type waste and earth had been dumped in the OEPA authorized excavation of May 11, 1976; a pile of unknown white bulk material had been dumped recently; a leachate was noted seeping from near the buried lagoon area; and drums were stacked near the creek which runs through the landfill. The drums were filled with a white colored semisolid. Several drums were leaking and had drained into a nearby creek; Mr. Skinner stated that the material was used for dust control on his driveways.

Legal proceedings were initiated by the State of Ohio, against the Skinner Landfill operation, in the Butler County Court of Common Pleas (CCP) on August 22, 1977. In January of 1979, the CCP entered a final judgment, denying the Skinners any further chemical waste disposal at their landfill. The Court refused, however, to issue a mandatory injunction directing the Skinners to remove the accumulated wastes present on the site.

On August 1, 1979, the Butler County Court of Appeals affirmed the CCP judgment of January 1979, refusing to issue the mandatory injunction to remove present wastes on site. Twelve days later, on August 13, 1979, the OEPA requested that the Attorney General's Office appeal the Court of Appeals, First Appellate District of Ohio, decision in State of Ohio, ex rel. Ned E. Williams, et al., versus Albert Skinner and Mrs. Albert Skinner, dba The Skinner Landfill, No. CA79-02-0010, filed August 1, 1979. OEPA lost this appeal.

The Field Investigation Team (FIT) on September 10, 1980, attempted a site inspection, but were refused entrance by Mrs.

Skinner. On July 19, 1982, the FIT finally gained access and began drilling four monitoring wells as part of the Mitre Program (Hazardous Ranking System). The four monitoring wells were completed on July 22, 1982. Two of the wells were dry, and the other two were sampled on July 27, 1982. The FIT submitted their assessment to the U.S. EPA on September 3, 1982.

In April 1983, the U.S. EPA conducted a responsible party search of the Skinner Landfill. The Remedial (REM II) activities for Skinner Landfill undertaken by Roy F. Weston Inc., began in August 1984. On January 28, 1986, U.S. EPA Remedial Project Manager (RPM) Gene Wong, requested that the U.S. EPA Emergency Response Section perform a site assessment of the Skinner Landfill.

3.0 SITE INSPECTION

On February 13, 1986, On-Scene Coordinator (OSC) Ross Powers, and Technical Assistance Team (TAT) members Robert McLeod and Craig Bell met with RPM Gene Wong, OEPA representative Tom Onco, and Mark Hudson and Mike Bort of Roy F. Weston, (REM II project). Additionally, Mr. Skinner's son, Ray Skinner was present as an escort. TAT members air monitored the site with a photoionization detector (HNU) and a combustible gas indicator. Only the HNU readings exceeded background, which occurred during near contact with suspect material.

During the site inspection, it was noted that active demolition waste landfilling was occurring throughout the 78 acres of the Skinner Landfill. The site, well vegetated with mature trees, had four active residences within its confines (Figure 2). Partial fencing encompassed the site, however the landfill was easily accessible with off-road recreational vehicles entering the site often. Numerous underground storage tanks, junk vehicles, appliances, railroad cars, and demolition debris littered the site. The Skinners also have several pieces of heavy equipment, a rock crushing device, several storage buildings and an abandoned stacked burning pit on the site.

Supposedly, numerous drums on the site contained motor oil, grease and anti-freeze, which are used in the operation of heavy equipment. One group of drums, near Skinner Creek on the west side of the site, consisted of thirty-three 55-gallon drums marked "paint thinner", and sixty-three 5-gallon cans marked "roofing tar". These drums were in deteriorated condition, and several had degraded to the point of losing their contents. The other large collection of drums was at the north boundary in a heavily vegetated area. Here, approximately fifty 55-gallon drums were situated in a disorderly manner. Several of these drums were severely degraded and the contents solidified. These drums appeared to contain paint. All other drums and tanks on the

site, which contained materials, were identified by Mr. Ray Skinner to contain motor oils, grease and anti-freeze all used in the operation of the landfill.

Mr. Ray Skinner reported that he intended to move all the drummed material used in the landfill operation into locked railroad cars. Mr. Ray Skinner also stated that he intended to sell the tar and thinner located by Skinner Creek, and crush every empty steel drum on the landfill. The several large underground storage tanks present on the site were part of a scrap metal operation engaged in by Mr. Ray Skinner, and were open and appeared empty.

The site of both the buried lagoon and excavation of May 11, 1976, was heavily vegetated and partially covered by demolition debris. The four monitoring wells at the old lagoon site appeared to be in good condition. One empty electrical transformer was observed at the site.

On February 14, 1986, TAT members Bell and McLeod met OSC Powers and RPM Wong, at the Skinner Landfill to conclude the site inspection. Mr. Ray Skinner again accompanied the group during the inspection. The morning activities consisted of continuing to locate and identify drums and their contents. The drums located that day were either empty, or identified by Mr. Ray Skinner as containing material used in the operation of the landfill. At the end of the day, it was decided that a comprehensive sampling of the site would be carried out to characterize the site.

On February 19, 1986, TAT members Bell and McLeod met OSC Powers at Skinner Landfill. Mrs. Skinner refused entry, stating that her son was not available to escort the team. OSC Powers contacted the office of Regional Counsel who worked out an agreement to allow entry on February 20, 1986.

On February 20, 1986, TAT members Bell and McLeod, along with OSC Powers entered Skinner Landfill to collect samples. Mr. Ray Skinner accompanied the sampling team throughout the day.

Samples were collected to qualify potential surface problems, which included a pile of white material, drums on site, flooring blocks and a transformer. Additionally, sampling was used to identify off-site migration of contaminants. The areas identified as potential release points included seeps below the old waste lagoon, seeps below the landfilling operation, runoff from the landfill, and runoff from the old waste lagoon.

The first phase of the sampling involved bailing the monitoring wells and placing seep collectors in the stream bank. Upon completion of the aforementioned tasks, the pile of white

material identified as lime was sampled by pushing a hollow tube three feet into the material. The tube was then extracted and the cores of the samples composited. The sample was analyzed for metals, organics, ignitibility and reactivity.

Along Skinner Creek, the thirty-three 55-gallon drums marked "thinner", and sixty-three 5-gallon cans marked "roofing tar" had been removed by the property owner prior to the February 20 visit. A composite soil sample was collected from the spot where the drums had been placed. This sample was analyzed for volatile organic compounds (VOCs).

Of approximately fifty 55-gallon drums located on the north boundary of the landfill, a single drum was sampled. This sample was analyzed for VOCs and flashpoint. Open drums showed decay, and appeared to contain similar substances - i.e., paint.

A pile of flooring blocks on the site were sampled by breaking up several of the blocks and compositing the pieces. The samples were analyzed for polychlorinated biphenyls (PCBs). A composite soil sample was collected from around the base of an apparently empty transformer, and analyzed for PCBs.

To identify off-site contaminant migration, these samples were analyzed for metals and organics.

Two monitoring wells, situated at the site in the now buried lagoon, were sampled with a stainless bailer. The bailer was decontaminated between wells and the cord changed. The well samples were analyzed for metals and organics.

On March 14, 1986, TAT members Bell and McLeod returned to the Skinner Landfill, and sampled the four wells on the property. The wells were all potable water sources utilized by the Skinner family. The samples were analyzed for VOCs.

4.0 ANALYTICAL RESULTS

Analytical results are presented in the following: Table 1 from the February 20, 1986 liquid sampling, Table 2 from the February 20, 1986 well sampling, and Table 3 from the March 14, 1986 well sampling. Table 4 presents the list of compounds and elements detected at the Skinner Landfill with the associated referenced standards.

As illustrated in the three tables, many compounds and elements exceed the regulatory standards. The majority of these contaminants are Resource Conservation and Recovery Act (RCRA) regulated waste and therefore, are listed hazardous waste.

LEGEND

- ⊗ DEPRESSION
- ⌘ ELEVATED TERRIAN
- STORAGE BUILDING
- HOUSES

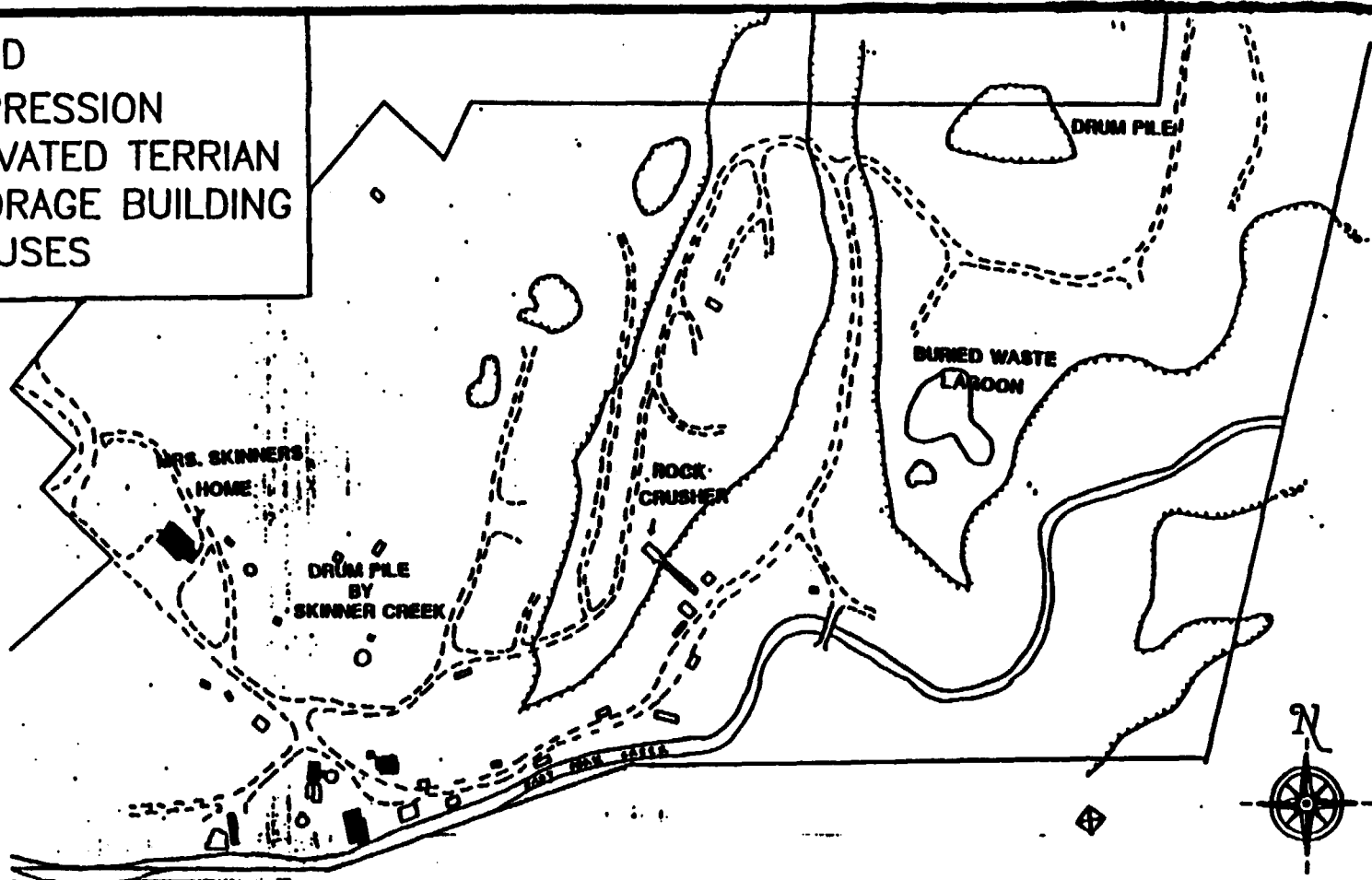


FIGURE 2
SITE MAP
SKINNER LANDFILL
WESTCHESTER, OHIO

NOT TO SCALE

WESTON
MANAGERS DESIGNERS/CONSULTANTS

DRAWN BY L.A.	DATE 6-9-88	PCS 1194
APPROVED J.B.	DATE 6-9-88	TDD 5870-27

TABLE 1
ANALYTICAL RESULTS OF SAMPLES COLLECTED BY THE THT*
AT SKINNER LANDFILL
WEST CHESTER, OHIO
FEBRUARY 20, 1986
(results in parts per billion)

CONTAMINANT	LAGOON SEEP #50	LAGOON RUNOFF #53	IMP SEEP #51	IMP RUNOFF #52	LIME LAGOON #1	NORTH EAST DRUM PILE #2	SOIL BY SKINNER CREEK #3
BENZENE	—	—	—	—	NA	15.07**	—
2-CHLOROETHYL VINYL ETHER	39.48	42.90	45.77	22.32	NA	—	3580.08
CHLOROFORM	3.67	—	4.84	2.19	NA	—	294.73
TRANS-1,3-DICHLOROETHENE	—	—	—	—	NA	—	4.61
ETHYL BENZENE	—	3.76	—	—	NA	3403.50**	11.39**
METHYLENE CHLORIDE	37.01	12.51	82.52	54.67	NA	—	—
TOLUENE	40.41	125.82	59.17	77.22	NA	3803.80**	—
1,1,1-TRICHLOROETHANE	39.19	52.15	31.85	33.79	NA	—	—
TRICHLOROETHENE	—	54.88	—	—	NA	—	—
ANTHRACENE	—	—	—	1.13	NA	NA	NA
BENZOPHENE	—	—	—	1.18	NA	NA	NA
EP Toxicity (results in ppm)							
ARSENIC	0.12**	—	0.007**	0.005**	0.001**	NA	NA
BARIUM	—	—	—	—	3.0**	NA	NA
CHROMIUM-TOTAL	0.33	—	0.13	—	—	NA	NA
COPPER	0.11	—	—	—	NA	NA	NA
LEAD	0.28	—	—	—	—	NA	NA
MERCURY	0.19	—	—	—	—	NA	NA
NICKEL	0.20	—	—	—	NA	NA	NA
ZINC	0.88	—	—	—	NA	—	NA
FLASH POINT	NA	NA	NA	NA	>212°F	82°F	NA

*Samples Analyzed by Suburban Laboratories, Inc., Hillside, Illinois

— Below Detection Limit

NA Not Analyzed

** Concentrations reported in parts per million

TABLE 2
ANALYTICAL RESULTS OF SAMPLES COLLECTED BY THE TAT*
AT SKINNER LANDFILL
WESTCHESTER, OHIO
FEBRUARY 20, 1986
(results in parts per billion)

CONTAMINANT	WELL #54	WELL #55D	WELL #56	FIELD BLANK
BENZENE	1163.39	1270.37	8.66	-
CHLOROBENZENE	62.49	75.46	-	-
CHLOROETHANE	288.61	343.38	-	-
CHLOROFORM	59.36	70.21	122.37	5.93
1,3 DICHLOROBENZENE	756.24	586.48	-	-
1,4 DICHLOROBENZENE	111.11	-	-	-
1,1 DICHLOROETHANE	1780.31	1963.23	-	-
1,2 DICHLOROETHANE	65.48	101.84	-	-
1,1 DICHLOROETHENE	20.43	35.66	22.97	-
TRANS 1,2 DICHLOROETHENE	788.32	968.22	-	-
1,2 DICHLOROPROPANE	805.54	1376.18	-	-
ETHYL BENZENE	181.40	215.82	7.30	-
METHYLENE CHLORIDE	295.06	516.79	1104.69	36.22
TOLUENE	3231.65	3393.95	381.62	44.79
1,1,1 TRICHLOROETHANE	176.75	274.89	293.65	24.06
TRICHLOROETHENE	25.01	14.73	29.02	-
PHENOL	14.10	-	-	-
2-CHLOROPHENOL	6.27	-	-	-
BIS (2-CHLOROETHYL) ETHER	315.61	313.18	-	-
BIS (2-ETHYHEXYL) PHTHALATE	32.34	61.78	4.68	1.10
NAPHTHALENE	12.38	16.25	-	-
ARSENIC	20.00	30.00	NA	-
ZINC	230.00	180.00	NA	-

* SAMPLES ANALYZED BY SUBURBAN LABORATORIES, INC, HILLISIDE, ILLINOIS
- Below Detection Limit
NA Not Analyzed

TABLE 3
ANALYTICAL RESULTS OF SAMPLES COLLECTED BY THE TAT*
AT SKINNER LANDFILL
WEST CHESTER, OHIO
March 14, 1986
(results in parts per billion)

CONTAMINANT	S61 LAGOON WELL	S62 SKINNER WELL	S64 FIELD BLANK
1,1 DICHLOROETHANE	3.00	—	—
1,2 DICHLOROPROPANE	5.00	—	—
1,1,1 TRICHLOROETHANE	20.00	14.00	—

* SAMPLES ANALYZED BY CANTON ANALYTICAL LABORATORY, INC,
YPSILANTI, MICHIGAN
— Below Detection Limit

TABLE 4
STANDARDS FOR CONTAMINANTS
FOUND AT SKINNER LANDFILL
(Concentrations in parts per billion)

CONTAMINANT	TLV/1	AQUATIC CRITERIA/2	HA ONE DAY/3	HA TEN DAYS/3	HA CHRONIC/3	CONC. IN NATURAL SOILS/4
BENZENE	30	5300	-	230	70	-
CHLOROBENZENE	350	3500	1800	1800	30000	-
CHLOROFORM	10000	1200	-	-	-	-
1,3 DICHLOROBENZENE	-	700	-	-	-	-
1,4 DICHLOROBENZENE	-	440	-	-	-	-
1,1 DICHLOROETHANE	-	-	-	-	-	-
1,2 DICHLOROETHANE	-	-	-	-	-	-
1,1 DICHLOROETHENE	-	-	1000	-	70	-
TRANS 1,2 DICHLOROETHENE	-	-	2700	270	-	-
1,2 DICHLOROPROPANE	-	2100	-	90	-	-
ETHYL BENZENE	435	560	-	-	-	-
METHYLENE CHLORIDE	350	-	13000	1500	150	-
TOLUENE	375	5200	21500	2200	340	-
1,1,1 TRICHLOROETHANE	-	-	-	-	1000	-
TRICHLOROETHENE	-	-	2000	200	75	-
PHENOL	19	3400	-	-	-	-
2-CHLOROPHENOL	-	180	-	-	-	-
NAPHTHALENE	50	-	-	-	-	-
ARSENIC	0.20	440	-	-	-	5000
BARIUM	-	-	-	-	-	430000
CHROM-TOTAL	-	21	1400	1400	-	100000
COPPER	0.20	-	-	-	-	30000
LEAD	-	-	-	-	-	10000
MERCURY	0.05	4.1	-	-	-	30
NICKEL	-	-	-	-	-	40000
ZINC	5.00	-	-	-	-	50000

1. Threshold Limit values established by the American Conference of Governmental Industrial Hygienists.
2. Federal Water Quality Criteria for Freshwater Aquatic Life (Acute).
3. Health Advisories (1-day, 10-day, chronic) established by the U.S. EPA Office of Drinking Water.
4. Average Element Concentrations in Natural soils adapted from Hazardous Waste Land Treatment, U.S. EPA, SW-874 (April, 1983).

5.0 THREATS TO HUMAN HEALTH AND THE ENVIRONMENT AS RELATED TO THE NATIONAL CONTINGENCY PLAN

The Skinner Landfill site has been found to pose the following actual and potential threats to human health and the environment as delineated in 40 CFR Section 300.65 (b)(2) of the National Contingency Plan:

- 1) Actual or potential exposure to hazardous substances, pollutants or contaminants by nearby populations, animals or the food chain;
- 2) Actual or potential contamination of drinking water supplies or sensitive ecosystems;
- 3) Hazardous substances or pollutants or contaminants in drums, barrels, tanks or bulk storage containers that may pose a threat of release to the environment; and
- 4) High levels of hazardous substances or pollutants or contaminants in soils largely at or near the surface, that may migrate.

5.1 Actual or Potential Exposure

The presence of the drums at the northeast corner of the site poses an existing threat of exposure. These drums, tentatively identified as "brilliantly colored paint", are randomly scattered, in various stages of decay, and currently leaking contents. Sample analysis indicates that these drums contain high concentrations of benzene, ethyl benzene and toluene. The status and condition of these drums presents an actual and potential threat to nearby populations, animals, and the food chain.

5.2 Actual or Potential Contamination

The sample data generated from the monitoring wells in the buried waste lagoon demonstrates the presence of elevated levels of chloroform, 1,3-dichlorobenzene, methylene chloride, toluene and 1,1,1-trichloroethane (1,1,1-TCA) in the ground water. However, analysis of water samples collected from the potable water wells on site show only three contaminants: 1,1-dichloroethane, 1,2-dichloropropane and 1,1,1,-TCA. These substances were present at levels not considered hazardous. The potential contamination of drinking water supplies does exist through migration of the contaminants in to the ground water, and may explain the presence of 1,1,1-TCA in both the monitoring wells and the potable water wells.

5.3 Threat of Release

In its current state, the drum pile at the northeast corner of the site has released contaminants, and poses a continuing threat of release as the drums decompose.

5.4 Threat of Migration

Surface soils collected next to Skinner Creek (where drums marked "thinner" had been stored) were analyzed, with results showing elevated levels of ethyl benzene and chloroform. The proximity of Skinner Creek to the contaminated surface soils offers a path of migration for contaminants.

6.0 RECOMMENDATIONS

Because Skinner Landfill is on the National Priorities List, and currently under investigation by the U.S. EPA Waste Management Division, Remedial Section, action by the Emergency Response Section is not warranted at this time. Based on the above threats, the TAT does recommend the following for implementation by the lead agency:

- ° establish a monitoring well sampling program in and around the landfill;
- ° remove contaminated soils for disposal or treatment; and,
- ° stage, sample, overpack, and dispose of drums located in the northeast section of the site.

**ROUND 1 AND 2 RI/FS SAMPLING
CONDUCTED IN 1986**

APPENDIX F

SAMPLING DATA TABLES

Table

F1	Volatile Organic Compounds -- Groundwater
F2	HVA Compounds -- Groundwater
F3	Pesticide/PCB Compounds -- Groundwater
F4	Inorganic Compounds -- Groundwater
F5	General Tests -- Groundwater
F6	Volatile Organic Compounds -- Surface Water
F7	Volatile Organic Compounds -- Sediment
F8	HVA Compounds -- Surface Water
F9	HVA Compounds -- Sediment
F10	Pesticide/PCB Compounds -- Sediment
F11	Inorganic Compounds -- Surface Water
F12	Inorganic Compounds -- Sediment
F13	General Tests -- Surface Water
F14	Volatile Organic Compounds -- Surface Soil
F15	HVA Compounds -- Surface Soil
F16	Pesticide/PCB Compounds -- Surface Soil
F17	Inorganic Compounds -- Surface Soil

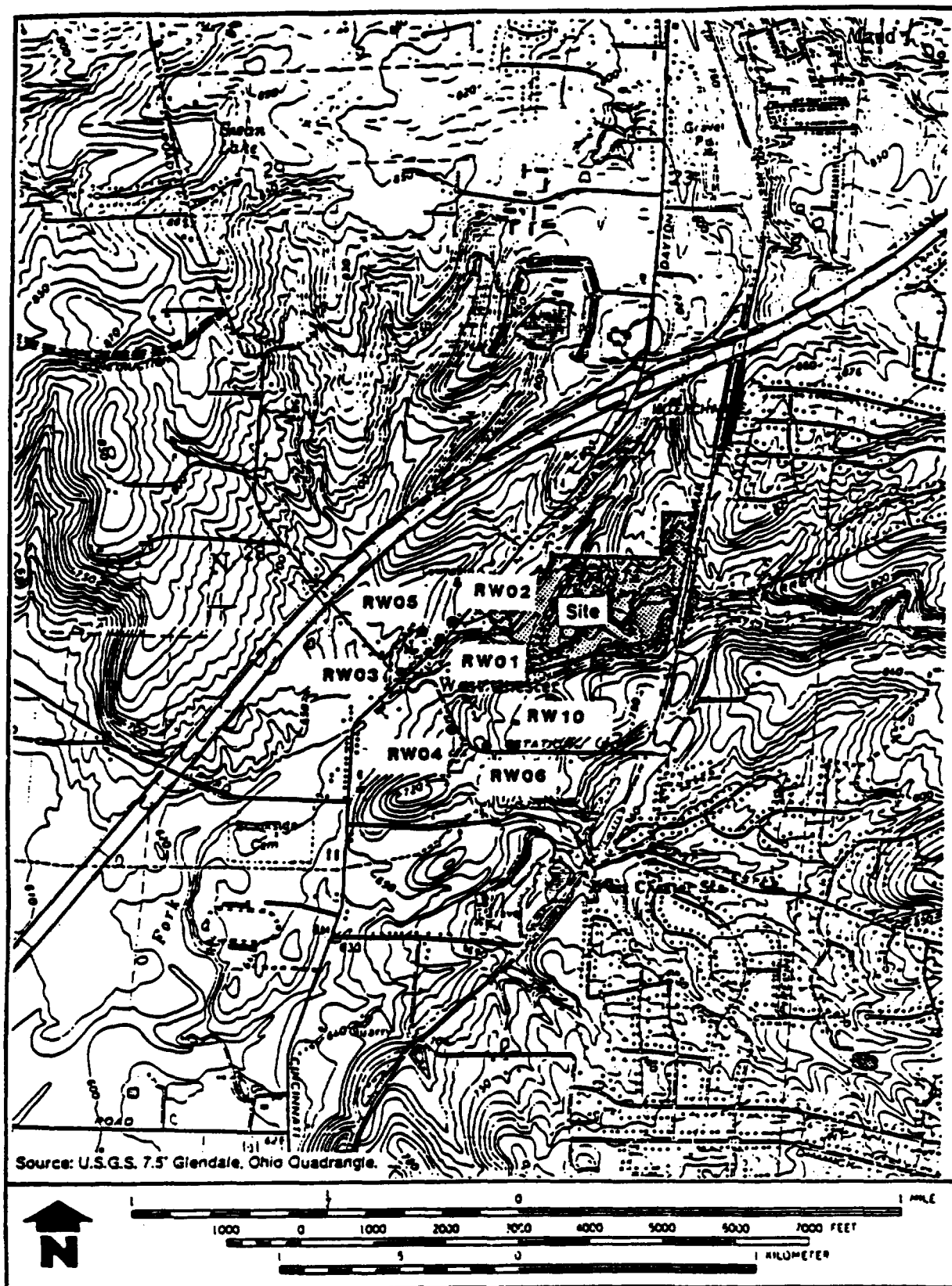


FIGURE 5-5 RESIDENTIAL WELL SAMPLING LOCATIONS

TABLE S-12

SUMMARY OF RESIDENTIAL WELL VOC ANALYSES
ALL VALUES IN ug/l (ppb)

	RW01	RW02	RW03	RW04	RW05	RW05DP	RW06	RW10	Field Blank	Maximum Contaminant Level (MCL)
1,1,1-Trichloroethane	---	---	---	---	---	---	---	---	9.0	200
Acetone	---	---	---	---	---	---	---	---	77	NE
Bromodichloromethane	---	---	5.0	---	---	---	---	---	---	100
Chloroform	---	---	8.0	---	---	---	---	---	---	100
Toluene	---	---	---	---	---	---	---	5.5	---	2000*
Methylene Chloride	---	---	---	---	---	---	---	10.0	---	NE

--- Not Detected

DP - Duplicate

NE - Not Established

* Recommended Maximum Contaminant Level (RMCL)

TABLE 5-13

SUMMARY OF RESIDENTIAL WELL BNA ANALYSES
ALL VALUES IN ug/l (ppb)

	RW01	RW02	RW03	RW04	RW05	RW05DP	RW06	RW10	Field Blank	Maximum Contaminant Level (MCL)
fluoranthene	---	2.0	---	---	---	---	---	---	---	NE
Pyrene	---	1.7	---	---	---	---	---	---	---	NE
Phenol	---	---	---	---	---	---	---	140	---	NE
4-Methylphenol	---	---	---	---	---	---	---	210	---	NE
Benzoic Acid	---	---	---	---	---	---	---	45	---	NE

--- Not Detected
DP - Duplicate
NE - Not Established

TABLE 5-14

SUMMARY OF RESIDENTIAL WELL PESTICIDE/PCB ANALYSES
ALL VALUES IN ug/l (ppb)

	RU01	RU02	RU03	RU04	RU05	RU05DP	RU06	RU10	Field Blank	Maximum Contaminant Level (MCL)
Lindane	---	---	---	---	---	---	0.060	---	---	NE
Heptachlor	---	---	---	---	---	---	0.060	---	---	0*
Heptachlor epoxide	---	---	0.060	0.060	0.060	0.060	---	---	---	0*
Endosulfan I	---	0.067	0.060	0.060	0.060	0.060	0.20	---	---	NE
Dieldrin	---	0.090	---	---	---	---	0.240	---	---	NE
Beta-BHC	---	---	---	---	---	---	---	10.5	---	NE
Delta-BHC	---	---	---	---	---	---	---	5.8	---	NE
4,4'-DDT	---	---	---	---	0.060	0.090	0.460	---	---	NE
Methoxychlor	---	---	---	---	---	---	0.520	---	---	NE
Aroclor 1245	---	---	---	---	0.20	0.20	---	---	---	0*

--- Not Detected

DP - Duplicate

* Proposed Value

TABLE 5-15

SUMMARY OF RESIDENTIAL WELL INORGANICS ANALYSES
SKINNER LANDFILL
ALL VALUES IN ug/l (ppb)

	RW01-01	RW02-01	RW03-01	RW04-01	RW05-01	RW05-DP	RW06-01	RW10-01	Field Blank	Primary Drinking Water Standards
Aluminum	---	98.2 K	---	---	92.6	88.3	45 K	2650	---	NE
Barium	50	633	48.0	50.4	120	118	592	184	---	1000
Boron	206	155	132	93.6	574	258	94.3	127	---	NE
Calcium	97.3 K	219 K	77.7 K	99.5 K	97.7 K	97.4 K	155 K	151 K	---	NE
Chromium	---	186	---	---	---	---	76.4	10.2	9.45 K	50
Copper	---	466	37.7	10.5	7.49	7.43	157	38.7	---	1000*
Iron	---	160 K	165	233	335	347	91.7 K	19.5 K	---	300*
Lithium	26.0	150	---	12.5	46.4	46.5	54.8	18.9	---	NE
Magnesium	27.0 K	58 K	11.6 K	---	26.8 K	26.7 K	33.6 K	29.2 K	---	NE
Manganese	31.8	2390	29.0	65.8	298	299	4020	667	---	50*
Potassium	---	14.9 K	3.04 K	---	---	---	6.14 K	62.7 K	---	NE
Sodium	18.0 K	4.96 K	11.5 K	---	148.0 K	148 K	3.12 K	11.4 K	---	NE
Strontium	1620	504	209	322	1340	1340	325	348	---	NE
Zinc	103	4910	298	858	894	887	1410	412	---	5000*
Alkalinity as CaCO ₃ (mg/l)	284	116	169	239	250	257	268	537	---	NE
Chloride (mg/l)	39	---	3	11	310	310	---	20	---	250*
Nitrate as Nitrogen (mg/l)	0.25	4.02	4.35	0.41	0.63	0.63	1.54	---	---	10
Sulfate (mg/l)	84	32	28	60	37	37	47	28	---	250*
Ammonia (mg/l)	---	---	---	---	---	---	---	---	---	NE

--- Not Detected

DP - Duplicate

* - Secondary drinking water standard.

K = Multiply Result by 1000

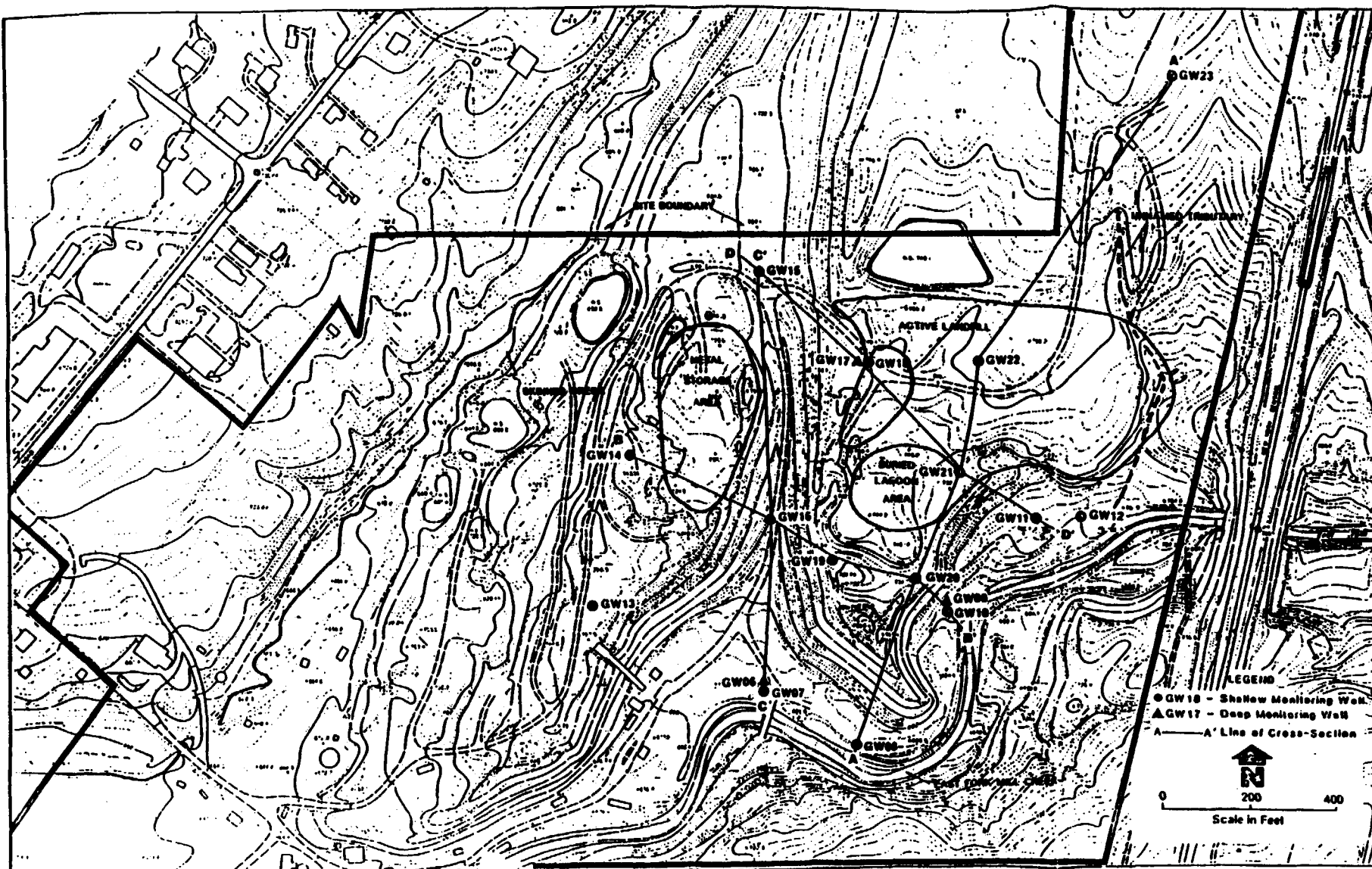


FIGURE 4-1 LOCATIONS OF GROUNDWATER MONITORING WELLS
AND GEOLOGIC CROSS-SECTIONS 4-3

TABLE F1
SUMMARY OF VOLATILE ORGANIC COMPOUND ANALYSES
GROUNDWATER SAMPLES
SKINNER LANDFILL

	GM06-01	GM06-02	GM07-01	GM07-02	GM08-01	GM08-0P	GM09-01	GM09-02	GM09-0P	
PHASE	1	2	1	1	1	1	1	2	1	
CRL LOG NUMBER	06RA01826	06RA01897	06RA01827	06RA01898	06RA01828	06RA01828	06RA01829	06RA02501	06RA01829	
TRAFFIC REPORT NUMBER	ENS18	EN295	ENS19	ENS43	ENS20	ENS21	ENS22	ENS46	ENS72	
DATE COLLECTED	05/23/06	06/21/06	05/23/06	06/21/06	05/19/06	05/19/06	05/15/06	06/21/06	05/16/06	
UNITS	UG/KG	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	
1,1,1-Trichloroethane	-----	-----	-----	-----	-----	-----	-----	-----	-----	
1,1-Dichloroethane	-----	-----	1 J	-----	-----	-----	-----	-----	-----	
2-Butanone	40 JB	-----	4 JB	-----	-----	4 JB	-----	-----	-----	
Acetone	500 B	15	12 B	-----	5 J	5 JB	-----	9.5 J	13 B	
Benzene	-----	1.6 J	-----	-----	-----	-----	-----	-----	-----	
Carbon Tetrachloride	-----	-----	-----	-----	-----	-----	-----	-----	-----	
Chlorobenzene	-----	-----	-----	-----	-----	-----	-----	-----	-----	
Chloroethane	-----	-----	-----	-----	-----	-----	-----	-----	-----	
Chloroform	-----	-----	-----	-----	-----	-----	-----	-----	-----	
Ethylbenzene	-----	-----	-----	-----	-----	-----	-----	-----	-----	
Methylene Chloride	15 JB	-----	6 B	-----	4 J	2 JB	-----	3.3 J	2 JB	
Tetrachloroethene	-----	-----	-----	-----	-----	-----	4 J	-----	1 J	
Toluene	-----	1.3 J	-----	-----	-----	-----	3 JB	1.3 J	1 JB	
Total Xylenes	-----	-----	-----	-----	-----	-----	-----	-----	-----	
Trans-1,2-Dichloroethene	-----	-----	27	11	-----	-----	-----	-----	-----	
Vinyl Chloride	-----	-----	4 J	-----	-----	-----	-----	-----	-----	

J = Estimated Value

B = Compound Detected in Lab Blank

TABLE F1 (cont'd)
SUMMARY OF VOLATILE ORGANIC COMPOUND ANALYSES
GROUNDWATER SAMPLES
SKINNER LANDFILL

	GM15-02	GM16-01	GM16-02	GM16-BK	GM17-01	GM17-02	GM17-BP	GM18-01	GM18-02	
PHASE	2	1	2	2	1	2	2	1	2	
CAL LOG NUMBER	06RAD2907	06RAD1836	06RAD2908	06RAD2909	06RAD1837	06RAD2909	06RAD2909	06RAD1838	06RAD2610	
TRAFFIC REPORT NUMBER	EMS76	EMS29	EMS77	EMS51	EMS30	EMS78	EMS47	EMS31	EMS79	
DATE COLLECTED	08/20/06	05/13/06	08/20/06	08/20/06	05/13/06	08/19/06	08/19/06	05/13/06	08/19/06	
UNITS	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	
1,1,1-Trichloroethane	-----	12	-----	2.6 J	-----	-----	-----	-----	-----	
1,1-Dichloroethane	-----	-----	-----	-----	-----	-----	-----	-----	-----	
2-Butanone	-----	-----	-----	-----	-----	-----	-----	36 J	-----	
Acetone	-----	2 J	-----	-----	14 J	-----	-----	-----	-----	
Benzene	-----	-----	-----	-----	340	-----	-----	950	-----	
Carbon Tetrachloride	-----	-----	-----	-----	-----	-----	-----	-----	-----	
Chlorobenzene	-----	-----	-----	-----	-----	-----	-----	-----	-----	
Chloroethane	-----	-----	-----	-----	-----	-----	-----	-----	-----	
Chloroform	-----	-----	-----	-----	-----	-----	-----	-----	-----	
Ethylbenzene	-----	-----	-----	-----	-----	-----	-----	-----	-----	
Methylene Chloride	-----	7	-----	5.6 B	14	-----	92 B	20 JB	-----	
Tetrachloroethene	-----	-----	-----	-----	20 J	-----	-----	-----	-----	
Toluene	3.8 JB	-----	3.8 JB	5.3 B	4 JB	3.6 JB	20 JB	-----	3.3 JB	
Total Xylenes	-----	-----	-----	-----	-----	-----	-----	-----	-----	
Trans-1,2-Dichloroethene	-----	-----	-----	-----	-----	-----	-----	-----	-----	
Vinyl Chloride	-----	-----	-----	-----	-----	-----	-----	-----	-----	

J = Estimated Value

B = Compound Detected in Lab Blank

TABLE F2
SUMMARY OF SEMIVOLATILE ORGANIC COMPOUND ANALYSES
GROUNDWATER SAMPLES
SKINNER LANDFILL

	1 GW07-02	1 GW08-0P	1 GW09-01	1 GW09-02	1 GW09-0P	1 GW10-01	1 GW10-02	1 GW11-01	1 GW11-02	1
PHASE	1 2	1 1	1 1	1 2	1 1	1 1	1 2	1 1	1 2	1
CRL LOG NUMBER	1 06RA01590	1 06RA01020	1 06RA01529	1 06RA02801	1 06RA01029	1 06RA01530	1 06RA02802	1 06RA01531	1 06RA02803	1
TRAFFIC REPORT NUMBER	1 EM543	1 EM521	1 EM522	1 EM546	1 EM572	1 EM523	1 EM540	1 EM524	1 EM549	1
	1	1	1	1	1	1	1	1	1	1
DATE COLLECTED	1 00/21/06	1 05/19/06	1 05/15/06	1 00/21/06	1 05/16/06	1 05/15/06	1 00/21/06	1 05/18/06	1 00/21/06	1
UNITS	1 UB/L	1	1 UB/L	1 UB/L	1 UB/L	1 UB/L	1 UB/L	1 UB/L	1 UB/L	1
1,4-Dichlorobenzene	-----	-----	-----	-----	-----	-----	-----	-----	-----	
2-Methylnaphthalene	-----	-----	-----	-----	-----	-----	-----	-----	-----	
4-Chloroaniline	-----	-----	-----	-----	-----	-----	-----	-----	-----	
4-Methylphenol	-----	-----	-----	-----	-----	-----	-----	-----	-----	
Benzoic Acid	-----	-----	-----	-----	-----	-----	-----	-----	-----	
Butylbenzylphthalate	-----	-----	-----	-----	-----	-----	-----	-----	-----	
Di-n-Butylphthalate	-----	-----	-----	-----	-----	-----	-----	3 J	-----	
Diethylphthalate	-----	-----	-----	-----	-----	-----	-----	-----	-----	
Methylene Chloride	-----	-----	-----	-----	-----	-----	-----	-----	-----	
N-Nitrosodiphenylamine	1.2 J	-----	-----	-----	-----	-----	-----	-----	-----	
Napthalene	-----	-----	-----	-----	-----	-----	-----	-----	-----	
Pentachlorophenol	-----	-----	-----	260	-----	-----	-----	-----	-----	
Phenol	-----	6 J	-----	-----	-----	-----	-----	-----	-----	
Tetrachloroethene	-----	-----	-----	-----	-----	-----	-----	-----	-----	
bis(2-Chloroethyl)Ether	-----	-----	-----	-----	-----	23 J	30	-----	-----	
bis(2-Chloroisopropyl)Ether	-----	-----	-----	-----	-----	-----	-----	-----	1.0 J	
bis(2-Ethylhexyl)Phthalate	5.4 JB	-----	3 J	21 JB	2 J	-----	-----	-----	-----	

J = Estimated Value

B = Compound Detected in Lab Blank

TABLE F2 (cont'd)
SUMMARY OF SEMIVOLATILE ORGANIC COMPOUND ANALYSES
GROUNDWATER SAMPLES
SKINNER LANDFILL

[illegible]

TABLE F3
SUMMARY OF PESTICIDE/PCB COMPOUND ANALYSES
GROUNDWATER SAMPLES
SKINNER LANDFILL

	1 08/06-02	1 08/16-02	1 08/17-02	1 08/17-02	1 08/17-02	1 08/18-02	1 08/20-02	1
PHASE	1 2	1 2	1 2	1 2	1 2	1 2	1 2	1
CRI LOG NUMBER	1 08/061597	1 08/062800	1 08/062809	1 08/062809	1 08/062810	1 08/062812	1	
TRAFFIC REPORT NUMBER	1 ERT95	1 800	1 ERT98	1 909	1 ERT97	1 ERT91	1	
	1	1	1	1	1	1	1	
DATE COLLECTED	1 08/21/06	1 08/20/06	1 08/19/06	1 08/19/06	1 08/19/06	1 08/20/06	1	
UNITS	1 08/L	1 08/L	1	1 08/L	1 08/L	1 08/L	1	
	0.13	---	---	---	---	---	---	
Dieldrin	---	0.04 J	0.02 J	0.03 J	0.02 J	---	---	
Hexachlorobenzene	---	---	---	---	---	---	---	
Hexachlorocyclopentadiene	---	---	---	---	---	0.04 J	---	

J = Estimated Value

Unfiltered Sample

PHASE	1	2	1	2	1	2	1	2	1	2	1	2
CRL LOG NUMBER	0606-01	0606-02	0607-01	0607-02	0608-01	0608-02	0609-01	0609-02	0610-01	0610-02	0611-01	0611-02
TRAFFIC REPORT NUMBER	WE1128	WE1150	WE1129	WE1151	WE1130	WE1130	WE1131	WE1131	WE1132	WE1132	WE1133	WE1133
DATE COLLECTED	05/23/06	06/21/06	05/23/06	06/21/06	05/19/06	05/19/06	05/19/06	05/19/06	05/19/06	05/19/06	05/15/06	05/15/06
UNITS	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L
Aluminum	773	67	---	49	13700	---	20000	---	---	---	---	---
Arsenic	---	---	---	---	8	---	16	---	---	---	---	---
Barium	100	70	109	96	93	56	144	56	41	---	---	---
Beryllium	---	---	---	---	---	---	---	---	---	---	---	---
Cadmium	63100	33700	126000	170000	193000	160000	316000	141000	9720	---	---	---
Chromium	23	---	---	6.1	21	---	31	---	---	---	---	---
Cobalt	---	---	---	---	---	---	---	---	---	---	---	---
Copper	---	7.7	---	10	40	---	37	---	2	---	---	---
Cyanide	---	---	---	---	---	---	---	---	---	---	---	---
Iron	596	47	55	67	22000	38	39200	33	---	---	---	---
Lead	---	---	4	---	14	8	24	4	---	---	---	---
Magnesium	8500	14000	22100	38000	30000	21000	49000	21500	16110	---	---	---
Manganese	---	18	378	2650	467	30	1120	30	---	---	---	---
Mercury	---	---	---	---	---	---	---	---	---	---	---	---
Nickel	---	---	---	16	26	---	40	---	---	---	---	---
Potassium	13200	50300	14500	11900	5100	1090	7100	1140	43150	---	---	---
Selenium	---	---	---	---	---	---	---	---	---	---	---	---
Sodium	52000	143000	29000	86600	10100	8510	12400	8310	30330	---	---	---
Vanadium	---	---	---	---	35	---	47	---	---	---	---	---
Zinc	10	5.7	---	19	94	11	139	---	2.1	---	---	---

TABLE F4 (cont'd)
SUMMARY OF INORGANIC COMPOUND ANALYSES
GROUNDWATER SAMPLES
SKINNER LANDFILL

	GW11-BKD	GW12-01	GW12-02	GW13-01	GW14-01	GW14-02	GW15-01	GW15-02	GW15-BP	
PHASE	1	1	2	1	1	2	1	2	2	
CRL LOG NUMBER	06RA01R31	06RA01R32	06RA02R04	06RA01R33	06RA01R34	06RA02R06	06RA01R35	06RA02R07	06RA02R07	
TRAFFIC REPORT NUMBER	NEJ105	NEJ135	NEJ150	NEJ136	NEJ137	NEJ161	NEJ130	NEJ101	NEJ153	
DATE COLLECTED	05/10/06	05/10/06	08/21/06	05/19/06	05/10/06	08/21/06	05/13/06	08/20/06	08/20/06	
UNITS	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	
Aluminum	-----	-----	92	-----	-----	43	-----	46	37	
Arsenic	-----	-----	-----	-----	-----	-----	-----	-----	-----	
Barium	-----	97	82	-----	-----	51	82	154	86	
Beryllium	-----	-----	-----	-----	-----	3.9	-----	-----	-----	
Calcium	-----	324200	274000	26000	48600	68400	136800	144000	166000	
Chromium	-----	6	7	-----	-----	4.3	-----	-----	15	
Cobalt	-----	7	9.1	-----	-----	-----	5	-----	-----	
Copper	-----	4	15	-----	-----	9.3	-----	7.9	8.5	
Cyanide	-----	-----	-----	-----	-----	-----	-----	-----	-----	
Iron	50	-----	137	84	154	47	787	46	35	
Lead	-----	-----	-----	8	4	-----	-----	-----	-----	
Magnesium	-----	105100	99500	18500	143000	18300	28610	23000	38100	
Manganese	-----	749	3130	33	39	59	2213	830	2340	
Mercury	-----	-----	-----	-----	-----	-----	0.2	-----	-----	
Nickel	-----	44	45	-----	-----	-----	-----	-----	13	
Potassium	-----	101000	48700	7410	1000	1700	5847	2200	11400	
Selenium	-----	-----	-----	-----	-----	-----	-----	-----	-----	
Sodium	-----	248400	184000	286000	6650	12200	76060	28600	79400	
Vanadium	-----	-----	-----	-----	-----	-----	-----	-----	-----	
Zinc	-----	1	58	-----	-----	9.8	10	7.8	26	

U = Unfiltered Sample

TABLE F4 (cont'd)
SUMMARY OF INORGANIC COMPOUND ANALYSES
GROUNDWATER SAMPLES
SKINNER LANDFILL

	BN19-01B	BN19-02	BN20-01	BN20-01B	BN20-02	BN21-01	BN21-01B	BN22-01	BN22-02	
PHASE	1	2	1	1	2	1	1	1	2	
CRL LOG NUMBER	BARA01839	BARA02511	BARA01840	BARA01840	BARA02512	BARA01841	BARA01841	BARA01842	BARA02514	
TRAFFIC REPORT NUMBER	NEJ142	NEJ190	NEJ144	NEJ144	NEJ191	NEJ145	NEJ145	NEJ146	NEJ990	
			U			U				
DATE COLLECTED	05/22/06	08/20/06	05/22/06	05/22/06	08/20/06	05/19/06	05/19/06	05/13/06	08/19/06	
UNITS	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	
Aluminum	-----	75	45700	-----	545	26000	-----	-----	323	
Arsenic	-----	-----	51	19	32	17	8	-----	-----	
Barium	50	90	694	957	1000	236	161	84	220	
Beryllium	-----	-----	-----	-----	-----	-----	-----	-----	-----	
Calcium	44000	113000	433000	160000	401000	385000	119300	90890	104000	
Chromium	8	6.1	101	-----	6	41	-----	19	31	
Cobalt	-----	-----	57	-----	18	35	-----	4	10	
Copper	-----	4.2	163	-----	3.5	59	-----	-----	6.3	
Cyanide	-----	-----	-----	-----	-----	-----	-----	-----	-----	
Iron	39	70	105000	5270	61800	50600	4320	73400	45300	
Lead	-----	-----	79	4	-----	27	5	-----	5.8	
Magnesium	28500	34600	109000	57200	72300	71300	35100	11890	19400	
Manganese	33	182	2570	603	3830	3180	1530	520	696	
Mercury	-----	-----	-----	-----	-----	-----	-----	-----	-----	
Nickel	-----	-----	150	25	40	71	-----	-----	20	
Potassium	2800	4220	31400	22100	36000	53000	44300	5929	18600	
Selenium	-----	-----	-----	-----	-----	-----	-----	-----	-----	
Sodium	4630	3900	82200	86300	83200	42800	44000	17100	63200	
Vanadium	-----	-----	102	-----	-----	61	-----	-----	-----	
Zinc	-----	6.6	441	-----	60	150	-----	10	47	

U Unfiltered Sample

TABLE F5
SUMMARY OF GENERAL TESTS ANALYSES
GROUNDWATER SAMPLES
SKINNER LANDFILL

	GU07-02	GU08-01	GU08-0P	GU09-02	GU10-01	GU10-02	GU11-01	GU11-02	GU12-02	
PHASE	1	1	1	2	1	2	1	2	2	
CRL LOG NUMBER	B6RA01898	B6RA01828	B6RA01828	B6RA02802	B6RA01830	B6RA02802	B6RA01831	B6RA02803	B6RA02804	
TRAFFIC REPORT NUMBER	NEJ151	2207E-01	2207E-02	NEJ154	2207E-03	NEJ154	2207E-04	NEJ157	NEJ158	
DATE COLLECTED	08/21/06	05/19/06	05/19/06	08/21/06	05/15/06	08/21/06	05/18/06	08/21/06	08/21/06	
UNITS	MG/L	MG/L	MG/L	MG/L	MG/L	MG/L	MG/L	MG/L	MG/L	
Alkalinity as CaCO3	1270	-----	-----	327	-----	2610	-----	1040	1360	
Ammonia as Nitrogen	-----	-----	-----	4.4	-----	20	-----	16	13	
Chloride	42	-----	-----	46	-----	200	-----	270	220	
Nitrate as Nitrogen	0.15	-----	-----	-----	-----	0.5	-----	0.35	4.1	
Sulfate	90	-----	-----	16	-----	80	-----	360	540	
TSS	-----	1890	1944	-----	986	-----	269	-----	-----	

TABLE F5 (cont'd)
SUMMARY OF GENERAL TESTS ANALYSES
GROUNDWATER SAMPLES
SKINNER LANDFILL

	06/20/01	06/20/02	06/21/01	06/22/02
PHASE	1 1	1 2	1 1	1 2
CRL LOG NUMBER	010001810	010002012	010001811	010002514
TRAFFIC REPORT NUMBER	2207E-07	NEJ191	2207E-08	NEE990
	1	1	1	1
DATE COLLECTED	05/22/06	08/20/06	05/19/06	08/19/06
UNITS	1 MG/L	1 MG/L	1 MG/L	1 MG/L
Alkalinity as CaCO3	-----	3040	-----	11000
Ammonia as Nitrogen	-----	36	-----	3.5
Chloride	-----	940	-----	82
Nitrate as Nitrogen	-----	-----	-----	-----
Sulfate	-----	-----	-----	37
TSS	2040	-----	3690	-----

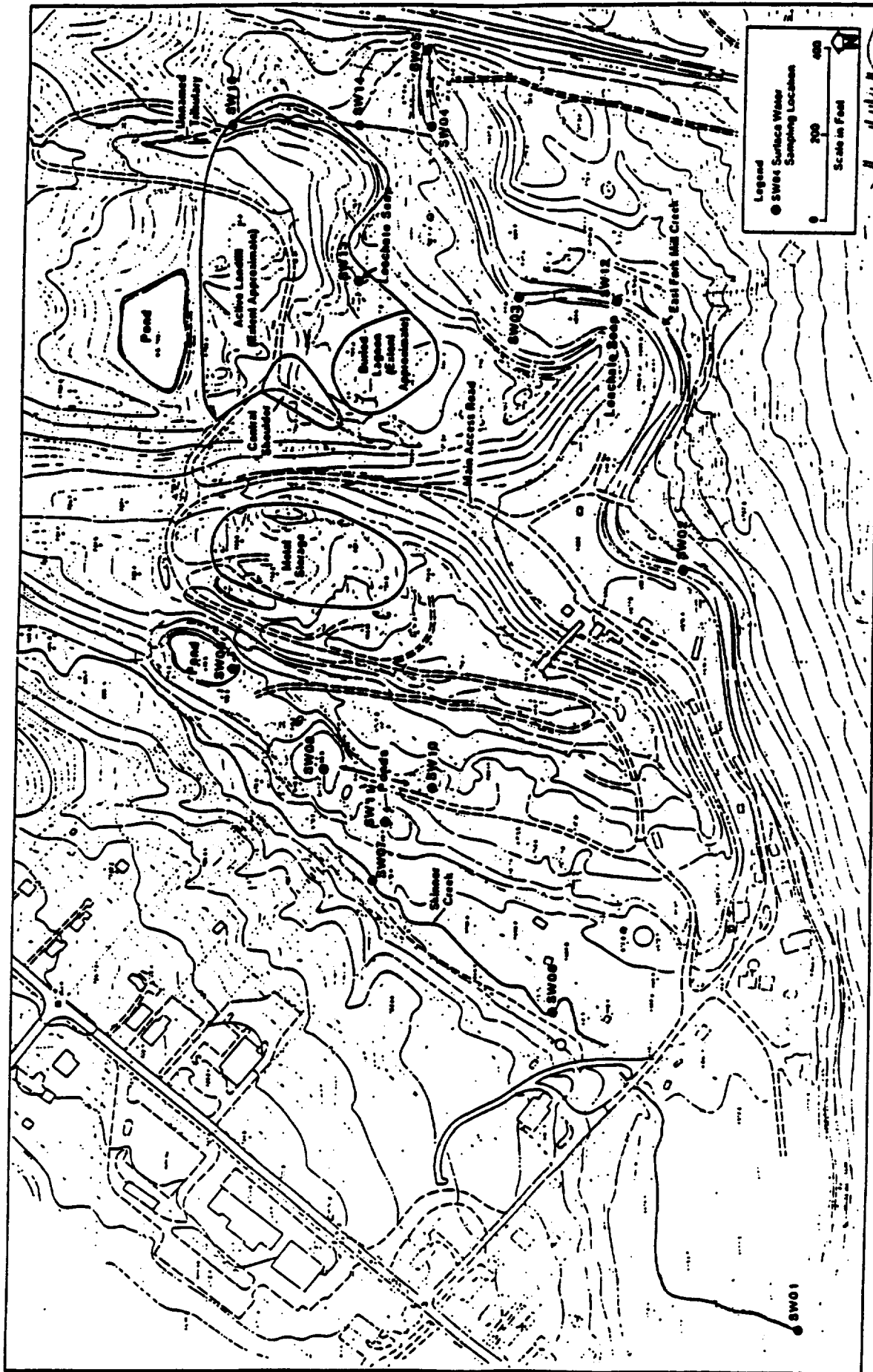


FIGURE 2-3 SURFACE WATER SAMPLE LOCATIONS

FIGURE 2-4 SEDIMENT SAMPLE LOCATIONS

TABLE F6
SUMMARY OF VOLATILE ORGANIC COMPOUND ANALYSES
SURFACE WATER SAMPLES
SKINNER LANDFILL

	SW01-01	SW02-01	SW03-01	SW04-01	SW05-01	SW06-01	SW07-01	SW07-BK	SW07-DP	
PHASE	1	1	1	1	1	1	1	1	1	
CRL LOG NUMBER	06RA01854	06RA01856	06RA01858	06RA01860	06RA01862	06RA01864	06RA01866	06RA01868	06RA01866	
TRAFFIC REPORT NUMBER	EN552	EN553	EN554	EN555	EN556	EN557	EN558	EN571	EN559	
DATE COLLECTED	05/04/06	05/04/06	05/04/06	05/04/06	05/04/06	05/05/06	05/05/06	05/07/06	05/05/06	
UNITS	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	
1,1,1-Trichloroethane	-----	-----	-----	-----	-----	-----	-----	0.3 J	-----	
1,1-Dichloroethane	-----	-----	-----	-----	-----	-----	-----	-----	-----	
2-Butanone	0.5 JB	0.2 JB	5.0 JB	7.5 JB	7.0 JB	6.7 JB	7.3 JB	0.5 JB	7.6 JB	
4-Methyl-2-Pentanone	-----	-----	-----	-----	-----	-----	-----	0.1 JB	-----	
Acetone	14.4 B	14.3 B	13.6 B	13.7 B	10.2 B	12.4 B	12.0 B	14.0 B	13.2 B	
Benzene	-----	-----	-----	-----	-----	-----	-----	0.1 J	-----	
Bromodichloroethane	-----	-----	-----	-----	-----	-----	-----	2.3 J	-----	
Bromoform	-----	-----	-----	-----	-----	-----	-----	1.7 J	-----	
Carbon Disulfide	0.3 J	-----	-----	-----	-----	-----	-----	-----	-----	
Chloroethane	-----	-----	-----	-----	-----	-----	-----	-----	-----	
Chloroform	-----	-----	-----	-----	-----	-----	-----	3.0 J	-----	
Dibromochloroethane	-----	-----	-----	-----	-----	-----	-----	3.2 J	-----	
Methylene Chloride	14.2 B	6.2 B	0.3 B	10.0 B	15.4 B	4.5 JB	0.3 B	11.1 B	10.3 B	
Toluene	-----	-----	-----	-----	0.5 J	-----	-----	1.4 J	-----	
Trans-1,2-Dichloroethene	-----	-----	-----	-----	-----	-----	-----	-----	-----	

J = Estimated Value

B = Compound Detected in Lab Blank

TABLE F6 (cont'd)
SUMMARY OF VOLATILE ORGANIC COMPOUND ANALYSES
SURFACE WATER SAMPLES
SKINNER LANDFILL

	1	8015-01	1
PHASE	1	1	1
CNL LOG NUMBER	1	000001875	1
TRAFFIC REPORT NUMBER	1	EN369	1
	1		1
DATE COLLECTED	1	05/07/06	1
UNITS	1	UG/L	1
1,1,1-Trichloroethane	-----		
1,1-Dichloroethane	-----		
2-Butanone	-----		
4-Methyl-2-Pentanone	-----		
Acetone	B	JB	
Benzene	-----		
Bromodichloroethane	-----		
Bromoform	-----		
Carbon Disulfide	-----		
Chloroethane	-----		
Chloroform	-----		
Dibromochloroethane	-----		
Methylene Chloride	7	B	
Toluene	-----		
Trans-1,2-Dichloroethane	-----		

J = Estimated Value

B = Compound Detected in Lab Blank

TABLE F7
SUMMARY OF VOLATILE ORGANIC COMPOUND ANALYSES
SEDIMENT SAMPLES
SKINNER LANDFILL

	5801-01	5802-01	5803-01	5803-BP	5804-01	5805-01	5806-01	5807-01	5807-BP
PHASE	I I	I I	I I	I I	I I	I I	I I	I I	I I
CRL LOG NUMBER	06RA01877	06RA01878	06RA01879	06RA01879	06RA01580	06RA01881	06RA01882	06RA01583	06RA01883
TRAFFIC REPORT NUMBER	EM540	EM541	EM542	EM586	EM587	EM588	EM589	EM590	EM591
DATE COLLECTED	05/04/86	05/04/86	05/04/86	05/05/86	05/04/86	05/04/86	05/05/86	05/05/86	05/05/86
UNITS	UG/KG	UG/KG	UG/KG	UG/KG	UG/KG	UG/KG	UG/KG	UG/KG	UG/KG
1,1,2,2-Tetrachloroethane	-----	-----	-----	-----	-----	-----	-----	-----	2.0 J
1,1-Dichloroethane	-----	-----	-----	-----	-----	-----	-----	-----	-----
2-Butanone	17.3 B	14.1 B	14.5 B	20.9 B	-----	14.9 B	13.6 JB	-----	24.5 B
2-Hexanone	-----	-----	-----	-----	-----	-----	-----	-----	5.1 J
4-Methyl-2-Pentanone	1.6 J	1.3 J	1.3 J	-----	1.1 J	1.0 JB	-----	-----	4.9 J
Acetone	32.7 B	22.4 B	30.3 B	34.2 B	34.8 B	22.6 B	20.9 B	22.0 B	-----
Benzene	-----	-----	-----	-----	-----	-----	-----	-----	-----
Carbon Disulfide	1.2 J	0.9 J	1.4 J	-----	0.4 J	1.3 JB	-----	0.8 JB	0.6 JB
Ethylbenzene	-----	-----	-----	-----	-----	-----	-----	-----	-----
Methylene Chloride	43.5 B	31.7 B	27.2 B	40.1 B	23.9 B	22.4 B	21.4 B	14.7 B	17.9 B
Toluene	-----	-----	-----	-----	-----	0.7 JB	0.5 JB	0.5 JB	0.6 JB
Total Xylenes	-----	-----	-----	-----	-----	-----	-----	-----	-----
Trichloroethene	-----	-----	-----	-----	-----	-----	-----	-----	-----

J = Estimated Value

B = Compound Detected in Lab Blank

TABLE F8
SUMMARY OF SEMI-VOLATILE ORGANIC COMPOUND ANALYSES
SURFACE WATER SAMPLES
SKINNER LANDFILL

	SM01-01	SM02-01	SM03-01	SM04-01	SM05-01	SM06-01	SM07-01	SM07-BK	SM07-BP	
PHASE										
COL. LOG NUMBER	04RA01034	04RA01034	04RA01038	04RA01040	04RA01042	04RA01044	04RA01046	04RA01046	04RA01046	
TRAFFIC REPORT NUMBER	EM552	EM553	EM554	EM555	EM556	EM557	EM558	EM571	EM558	
DATE COLLECTED	05/04/06	05/04/06	05/04/06	05/04/06	05/04/06	05/05/06	05/05/06	05/07/06	05/05/06	
UNITS	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	
1,2-Dichlorobenzene	-----	-----	-----	-----	-----	-----	-----	-----	-----	
Butylbenzylphthalate	-----	-----	-----	0.1 J	-----	-----	-----	-----	-----	
Di-n-Butylphthalate	0.1 J	-----	-----	-----	0.1 J	-----	-----	-----	-----	
Di-n-Octylphthalate	-----	1.3 J	-----	-----	-----	-----	-----	-----	3.6 J	
Phenol	0.9 J	0.9 J	0.6 J	3.2 J	0.5 J	-----	-----	-----	-----	
bis(2-Chloroethyl)Ether	-----	-----	-----	-----	-----	-----	-----	-----	-----	
bis(2-Ethylhexyl)Phthalate	3.4 JB	81.6 B	1.2 JB	11.5 B	2.9 JB	16.0 B	14.0 B	1.9 JB	131.9 B	

J = Estimated Value

B = Compound Detected in Lab Blank

TABLE F9
SUMMARY OF SEMIVOLATILE ORGANIC COMPOUND ANALYSES
SEDIMENT SAMPLES
SKINNER LANDFILL

	SD01-01	SD02-01	SD03-01	SD03-0P	SD04-01	SD05-01	SD06-01
PHASE	1	1	1	1	1	1	1
CRL LOG NUMBER	86RA01577	86RA01578	86RA01579	86RA01579	86RA01580	86RA01581	86RA01582
TRAFFIC REPORT NUMBER	EHS40	EHS41	EHS42	EHS86	EHS87	EHS88	EHS89
DATE COLLECTED	05/04/86	05/04/86	05/04/86	05/05/86	05/04/86	05/04/86	05/05/86
UNITS	UG/KG	UG/KG	UG/KG	UG/KG	UG/KG	UG/KG	UG/KG
2-Methylnaphthalene	5.8 J	4.5 J	-----	2.0 J	-----	8.7 J	-----
4-Methylphenol	1554.2	16.5 J	21.0 J	90.6 J	14.7 J	276.5 J	10.5 J
Acenaphthene	-----	-----	-----	-----	-----	51.3 J	-----
Acenaphthylene	-----	18.4 J	-----	-----	-----	-----	-----
Anthracene	67.9 J	348.6 J	-----	96.4 J	-----	90.3 J	-----
Benzo(a)Anthracene	363.5 J	258.0 J	-----	47.6 J	-----	255.2 J	-----
Benzo(a)Pyrene	705.7	309.5 J	-----	-----	-----	464.4	8.4 J
Benzo(b)Fluoranthene	325.6 J	258.5 J	-----	36.6 J	-----	226.9 J	11.6 J
Benzo(g,h,i)Perylene	256.6 J	162.9 J	-----	-----	-----	143.5 J	-----
Benzo(k)Fluoranthene	338.0 J	198.9 J	-----	37.5 J	-----	179.4 J	14.6 J
Butylbenzylphthalate	-----	-----	-----	-----	-----	51.7 J	-----
Chrysene	433.2 J	275.4 J	-----	60.2 J	-----	276.4 J	-----
Di-n-Butylphthalate	153.6 JB	164.0 JB	110.8 JB	104.4 JB	60.1 JB	33.2 JB	35.4 JB
Dibenzo(a,h)Anthracene	-----	-----	-----	-----	-----	32.7 J	-----
Dibenzofuran	-----	-----	-----	-----	-----	25.1 J	-----
Diethylphthalate	33.0 J	42.9 J	51.7 J	33.5 J	28.1 J	29.1 J	21.0 J
Fluoranthene	796.7	591.5	-----	137.0 J	-----	606.8	31.3 J
Fluorene	28.9 J	27.1 J	-----	-----	-----	54.4 J	-----
Indeno(1,2,3-cd)Pyrene	211.1 J	147.3 J	-----	-----	-----	124.4 J	-----
Isophorone	-----	-----	-----	-----	8.2 J	-----	114.3 JB
N-Nitrosodiphenylamine	-----	-----	-----	-----	-----	2.4 J	-----
Napthalene	-----	-----	-----	-----	-----	12.9 J	-----
Nitrobenzene	-----	-----	-----	-----	-----	-----	-----
Phenanthrene	396.1 J	338.2 J	-----	90.5 J	-----	443.9	15.1 J
Phenol	139.7 J	55.0 J	59.6 J	95.5 J	45.6 J	84.4 JB	15.1 JB
Pyrene	721.2	517.9	-----	89.0 J	-----	461.3	21.7 J
bis(2-Ethylhexyl)Phthalate	108.4 JB	104.3 JB	73.7 JB	83.9 JB	65.4 JB	394.4 JB	107.6 JB

J = Estimated Value

B = Compound Detected in Lab Blank

TABLE F10
SUMMARY OF PESTICIDE/PCO COMPOUND ANALYSES
SEDIMENT SAMPLES
SKINNER LANDFILL

	8807-01	8807-0P	8809-01	8810-01	8813-01	
PHASE	11	11	11	11	11	1
CRL LOG NUMBER	88RA01883	88RA01883	88RA01885	88RA01886	88RA01889	1
TRAFFIC REPORT NUMBER	EN590	EN591	EN593	EN594	EN597	1
	1	1	1	1	1	1
DATE COLLECTED	05/05/86	05/05/86	05/05/86	05/07/86	05/07/86	1
UNITS	UG/KG	UG/KG	UG/KG	UG/KG	UG/KG	1
Aldrin	-----	-----	-----	-----	1.9 J	
Aroclor-1260	11.43 J	29.85 J	442.19	-----	-----	
Delta-BHC	-----	-----	-----	0.5 J	-----	
Dieldrin	-----	-----	-----	-----	4.2 J	
Endrin Ketone	-----	-----	-----	-----	24.1	

J = Estimated Value

TABLE F11
SUMMARY OF INORGANIC COMPOUND ANALYSES
SURFACE WATER SAMPLES
SKINNER LANDFILL

	SW01-01	SW02-01	SW03-01	SW04-01	SW05-01	SW06-01	SW07-01	SW07-BK	SW07-BP
PHASE	1	1	1	1	1	1	1	1	1
CIL LOG NUMBER	04001654	04001656	04001658	04001660	04001662	04001664	04001666	04001668	04001669
TRAFFIC REPORT NUMBER	NEJ162	NEJ163	NEJ164	NEJ165	NEJ166	NEJ167	NEJ168	NEJ169	NEJ169
	1	1	1	1	1	1	1	1	1
DATE COLLECTED	05/04/06	05/04/06	05/04/06	05/04/06	05/04/06	05/05/06	05/05/06	05/07/06	05/05/06
UNITS	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L
Aluminum	260	336	111	261	299	128	192	300	182
Arsenic	---	---	---	---	---	---	---	---	---
Barium	113	48	43	47	47	39	40	31	41
Beryllium	---	---	---	---	---	---	---	---	---
Calcium	98900	91300	90300	98000	92400	121000	124000	37000	127000
Chromium	---	12	---	---	---	---	---	---	---
Copper	---	---	---	---	---	---	---	---	---
Iron	39	364	118	246	238	96	187	416	145
Lead	1.3	1.2	---	---	1.4	1.0	---	---	---
Magnesium	28400	31900	31000	29900	28000	22900	22000	10600	22000
Manganese	67	15	7	15	15	35	39	68	40
Mercury	0.3	---	---	---	---	---	---	---	---
Nickel	---	---	---	---	---	---	---	---	---
Potassium	3260	4286	2300	2770	---	2220	3180	---	3110
Silver	---	---	---	---	---	---	---	---	---
Sodium	28100	26700	26200	24500	24900	41100	42000	1630	44400
Tin	---	---	---	---	---	---	41	54	51
Zinc	---	22	---	---	---	---	---	---	---

TABLE F12
SUMMARY OF INORGANIC COMPOUND ANALYSES
SEDIMENT SAMPLES -
SKINNER LANDFILL

	8801-01	8802-01	8803-01	8803-BP	8804-01	8805-01	8806-01	8807-01	8807-BP
PHASE									
CAL LOG NUMBER	88A01877	88A01878	88A01879	88A01879	88A01880	88A01881	88A01882	88A01883	88A01883
TRAFFIC REPORT NUMBER	NEJ193	NEJ194	NEJ195	NEJ196	NEJ197	NEJ198	NEJ199	NEJ200	NEE977
DATE COLLECTED	05/04/86	05/04/86	05/04/86	05/05/86	05/04/86	05/04/86	05/05/86	05/05/86	05/05/86
UNITS	MG/KG	MG/KG	MG/KG	MG/KG	MG/KG	MG/KG	MG/KG	MG/KG	MG/KG
Aluminum	8890	3200	9020	12600	7090	4940	11600	8840	10000
Antimony	46	34	44	46	49	31	-----	42	46
Arsenic	-----	4.0	8.6	9.0	7.9	7.4	10	8.9	10.2
Barium	143	35.0	62	100	36.0	36	96	97	83
Beryllium	-----	-----	-----	-----	-----	-----	-----	-----	-----
Cadmium	-----	-----	4	5	-----	-----	4	-----	-----
Calcium	77200	242000	121000	47000	120000	123000	22300	63500	52100
Chromium	15	12	17	20	14	9	15	13	14
Cobalt	22	11	17	21	14	13	16	23	22
Copper	18	12	21	21	14	11	20	17	19
Iron	24100	13600	26400	29800	18600	15100	23400	21300	23800
Lead	43	12	14	12	7	12	21	46	46
Magnesium	9020	33200	16800	16500	22700	21000	5050	5050	5990
Manganese	2330	1020	711	899	730	694	803	1800	1400
Nickel	26	16	26	34	22	-----	23	24	26
Potassium	-----	1350	-----	-----	-----	-----	1850	-----	-----
Sodium	240	250	198	158	177	226	213	245	259
Tin	46	32	35	33	30	-----	-----	40	52
Vanadium	22	-----	18	23	16	14	20	20	18
Zinc	82	29	100	79	46	40	57	76	88

TABLE F13
SUMMARY OF GENERAL TESTS ANALYSES
SURFACE WATER SAMPLES
SKINNED LANDFILL

	8401-01	8401-02	8407-02	8403-01	8403-02	8403-0P	8404-01	8404-02	8405-01
PHASE	I	I	I	I	I	I	I	I	I
CRL LOG NUMBER	84001554	84001555	84001557	84001558	84001559	84001559	84001560	84001561	84001562
TRAFFIC REPORT NUMBER	2750E-1	2750E-9	2750E-10	2750E-3	2750E-11	2750E-12	2750E-4	2750E-13	2750E-5
	I	I	I	I	I	I	I	I	I
DATE COLLECTED	05/04/06	05/08/06	05/08/06	05/04/06	05/08/06	05/08/06	05/04/06	05/08/06	05/04/06
UNITS	MG/L	MG/L	MG/L	MG/L	MG/L	MG/L	MG/L	MG/L	MG/L
TSS	2.8	12.1	27.3	4.1	25.4	25.2	3.0	31.5	3.6

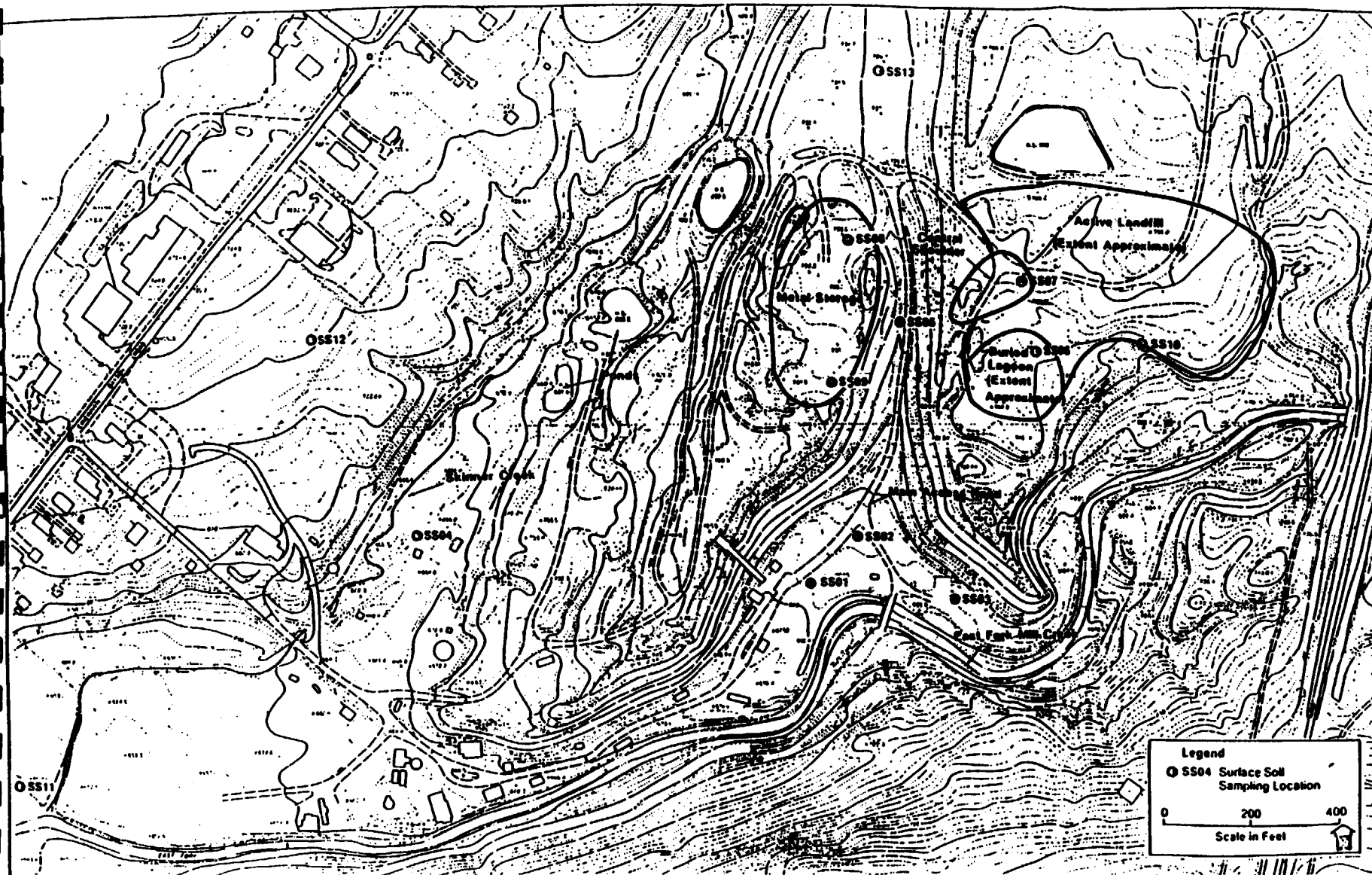


FIGURE 2-5 SURFACE SOIL
SAMPLING LOCATIONS

TABLE F14
SUMMARY OF VOLATILE ORGANIC COMPOUND ANALYSES
SURFACE SOIL SAMPLES
SKINNER LANDFILL

	SS02-01	SS04-01	SS04-02	SS04-0P	SS05-01	SS05-02	SS06-01	SS06-02	SS08-01	
PHASE	I I	I I	I I	I I	I I	I I	I I	I I	I I	I
CRL LOG NUMBER	B6RA01804	B6RA01807	B6RA01808	B6RA01809	B6RA01809	B6RA01810	B6RA01811	B6RA01812	B6RA01815	I
TRAFFIC REPORT NUMBER	EN220	EN223	EN224	EN225	EN226	EN501	EN502	EN503	EN506	I
	I	I	I	I	I	I	I	I	I	I
DATE COLLECTED	04/30/86	04/30/86	04/30/86	04/30/86	04/30/86	04/30/86	04/30/86	04/30/86	05/01/86	I
UNITS	UG/KG	UG/KG	UG/KG	UG/KG	UG/KG	UG/KG	UG/KG	UG/KG		I
1,1,1-Trichloroethane	-----	-----	-----	-----	-----	4.9 J	-----	-----	-----	
2-Butanone	-----	-----	31 J	-----	-----	-----	-----	-----	-----	
Acetone	13 J	11 J	11 J	0.9 J	9.7 J	-----	14	14	-----	
Benzene	2.2 J	-----	-----	-----	1.0 J	0.72 J	-----	-----	-----	
Carbon Disulfide	-----	-----	-----	-----	-----	-----	-----	-----	-----	
Methylene Chloride	-----	-----	-----	-----	-----	6.6 J	-----	6.4 J	1.4 J	
Tetrachloroethene	-----	-----	-----	-----	-----	2.1 J	-----	-----	-----	
Toluene	0	-----	-----	-----	-----	2.6 J	-----	3.0 J	-----	

J = Estimated Value

TABLE P15
SUMMARY OF SEMI-VOLATILE ORGANIC COMPOUND ANALYSES
SURFACE SOIL SAMPLES
KILMER LANDFILL

PHASE	5501-01	5501-02	5502-01	5502-02	5503-01	5503-02	5505-01	5505-02	5506-02	
CRL LOG NUMBER	060001001	060001002	060001003	060001004	060001005	060001006	060001007	060001010	060001012	
TRAFFIC REPORT NUMBER	EX217	EX218	EX219	EX220	EX221	EX222	EX226	EX501	EX503	
DATE COLLECTED	01/30/06	01/30/06	01/30/06	01/30/06	01/30/06	01/30/06	01/30/06	01/30/06	01/30/06	01/30/06
UNIT	UG/KG	UG/KG	UG/KG	UG/KG	UG/KG	UG/KG	UG/KG	UG/KG	UG/KG	UG/KG
Acenaphthylene	---	---	---	---	---	---	---	---	---	---
Anthracene	---	---	---	---	340	---	---	---	---	---
Benz(a)anthracene	---	---	---	---	3100	120	4310	---	---	---
Benz(a)Pyrene	---	---	---	---	5600	---	---	---	---	---
Benz(b)fluoranthene	---	---	---	---	4600	220	6170	550	---	---
Benz(g,h,i)Perylene	---	---	---	---	470	---	---	---	---	---
Benz(k)fluoranthene	760	210	---	---	460	---	---	---	---	---
Butylbenzylphthalate	---	---	---	---	7000	---	---	---	---	---
Chrysene	650	100	---	---	270	170	5560	500	---	---
Di-n-Butylphthalate	---	---	---	---	---	---	---	---	---	---
Di-n-Octylphthalate	---	---	---	---	---	---	---	---	---	---
Fluoranthene	600	120	1400	200	4000	---	7900	350	---	---
Hexachlorobenzene	---	---	---	---	---	---	23000	---	---	---
Indene(1,2,3-cd)Pyrene	---	---	---	320	1500	---	---	---	---	---
n-Hexadecylphenylamine	---	---	---	---	---	---	---	---	---	---
Phenanthrene	---	---	750	---	3100	100	4200	---	---	---
Pyrene	630	130	1240	230	3600	---	8500	490	---	---
bis(2-Ethylhexyl)Phthalate	---	190	---	---	1500	---	1710	---	160	---

Estimated Value

TABLE F16
SUMMARY OF PESTICIDE/PCD COMPOUND ANALYSES
SURFACE SOIL SAMPLES
SKINNER LANDFILL

	1 8807-01	1 8807-02	1
PHASE	1 1	1 1	1
CNL LOG NUMBER	1 00001813	1 00001814	1
TRAFFIC REPORT NUMBER	1 ENS04	1 ENS05	1
	1	1	1
DATE COLLECTED	1 03/01/00	1 03/01/00	1
UNITS	1 US/KG	1 US/KG	1
Arceles-1254	900	900	

TABLE F17
SUMMARY OF INORGANIC COMPOUND ANALYSES
SURFACE SOIL SAMPLES
SKINNER LANDFILL

	SS01-01	SS01-02	SS02-01	SS02-02	SS03-01	SS03-02	SS04-01	SS04-02	SS04-0P
PHASE	1	1	1	1	1	1	1	1	1
CRL LOG NUMBER	06RA01001	06RA01002	06RA01003	06RA01004	06RA01005	06RA01006	06RA01007	06RA01008	06RA01009
TRAFFIC REPORT NUMBER	NEJ101	NEJ102	NEJ103	NEJ104	NEJ105	NEJ106	NEJ107	NEJ108	NEJ109
DATE COLLECTED	04/30/06	04/30/06	04/30/06	04/30/06	04/30/06	04/30/06	04/30/06	04/30/06	04/30/06
UNITS	MG/KG	MG/KG	MG/KG	MG/KG	MG/KG	MG/KG	MG/KG	MG/KG	MG/KG
Aluminum	4500	9040	7260	9610	6040	8290	10700	14700	14400
Antimony	-----	-----	-----	-----	-----	-----	-----	-----	-----
Arsenic	-----	9.1	6	6.0	-----	-----	-----	-----	-----
Barium	84	96	125	143	93	101	74	53	53
Beryllium	-----	-----	-----	0.65	-----	-----	-----	0.7	0.09
Cadmium	-----	-----	-----	-----	-----	-----	-----	-----	-----
Calcium	79000	73000	70500	66700	20000	0950	13200	34600	10100
Chromium	12	12	13	13	15	11	15	23	21
Cobalt	7.0	8.9	7.3	12	10	11	12	15	14
Copper	25	19	25	25	22	17	19	25	24
Cyanide	-----	-----	-----	-----	-----	-----	-----	-----	-----
Iron	21300	25200	21300	26900	16900	20200	27300	35000	39400
Lead	86	39	51	43	61	27	19	6.0	7.1
Magnesium	13600	12600	16000	5060	7460	2300	4470	8170	8040
Manganese	1190	1400	2270	2700	856	1570	1090	561	576
Mercury	-----	-----	-----	-----	-----	-----	-----	-----	-----
Nickel	10	22	19	20	17	14	21	31	33
Potassium	1310	1390	1120	1300	860	940	1250	2400	2020
Sodium	1020	903	-----	706	-----	-----	-----	753	698
Tin	-----	-----	-----	-----	-----	-----	-----	-----	-----
Vanadium	15	21	15	22	15	16	23	26	24
Zinc	114	79	96	70	196	82	62	76	81

TABLE F1/ (cont'd)
SUMMARY OF INORGANIC COMPOUND ANALYSES
SURFACE SOIL SAMPLES
SKINNER LANDFILL

	SS09-01	SS09-02	SS10-01	SS10-02	SS11-01	SS12-01	SS13-01
PHASE	I	I	I	I	I	I	I
CHL LOG NUMBER	06RA01S17	06RA01S18	06RA01S19	06RA01S20	06RA01S94	06RA01S95	06RA01S96
TRAFFIC REPORT NUMBER	NEJ119	NEJ120	NEJ121	NEJ122	NEJ987	NEJ988	NEJ989
DATE COLLECTED	05/01/06	05/01/06	05/01/06	05/01/06	05/01/06	05/01/06	05/01/06
UNITS	MG/KG	MG/KG	MG/KG	MG/KG	MG/KG	MG/KG	MG/KG
Aluminum	2570	2000	7830	13100	8020	9140	7600
Antimony	-----	-----	-----	-----	-----	-----	-----
Arsenic	-----	-----	11	15	8	8.9	6.7
Barium	9.2	7	197	109	73	112	124
Beryllium	-----	-----	0.9	-----	-----	0.66	0.7
Cadmium	-----	-----	-----	-----	-----	-----	-----
Calcium	210000	184000	37600	8400	88900	24900	3980
Chromium	11	6.7	13	18	11	14	11
Cobalt	-----	4.1	9.7	13	7.4	11	12
Copper	16	12	39	34	23	22	16
Cyanide	-----	-----	-----	-----	-----	-----	-----
Iron	10800	12000	61600	39700	21000	23300	17400
Lead	15	11	121	22	31	25	28
Magnesium	45600	40000	3640	4560	19400	3580	1620
Manganese	614	561	1580	1030	1020	1040	2090
Mercury	-----	-----	-----	-----	-----	-----	-----
Nickel	10	7.9	17	30	16	16	12
Potassium	671	634	1180	1660	1650	1420	1120
Sodium	1990	1890	698	804	936	-----	439
Tin	-----	-----	-----	-----	-----	-----	-----
Vanadium	8	8	20	29	18	23	21
Zinc	108	47	329	92	116	66	63

**ROUND 3 RI/FS SAMPLING
CONDUCTED IN 1987**



100 CORPORATE NORTH, STE. 101
BANNOCKBURN, ILLINOIS 60015
312-295-6020

LETTER OF TRANSMITTAL

DATE	1/26/89	JOB NO.	130-RII-RIEPT
ATTENTION	Mr. Fred Bartman		
RE	Skinner RI/FS R3.		

TO U. S. Environmental Protection Agency
230 S. Dearborn Street
Chicago, IL. 60604

WE ARE SENDING YOU ☐ Attached ☐ Under separate cover via _____ the following items:

- | | | | | |
|---|---------------------------------------|--------------------------------|----------------------------------|---|
| <input type="checkbox"/> Shop drawings | <input type="checkbox"/> Prints | <input type="checkbox"/> Plans | <input type="checkbox"/> Samples | <input type="checkbox"/> Specifications |
| <input type="checkbox"/> Copy of letter | <input type="checkbox"/> Change order | <input type="checkbox"/> _____ | | |

COPIES	DATE	NO.	DESCRIPTION
1	1/89		Round 3 Sampling Data Tables.

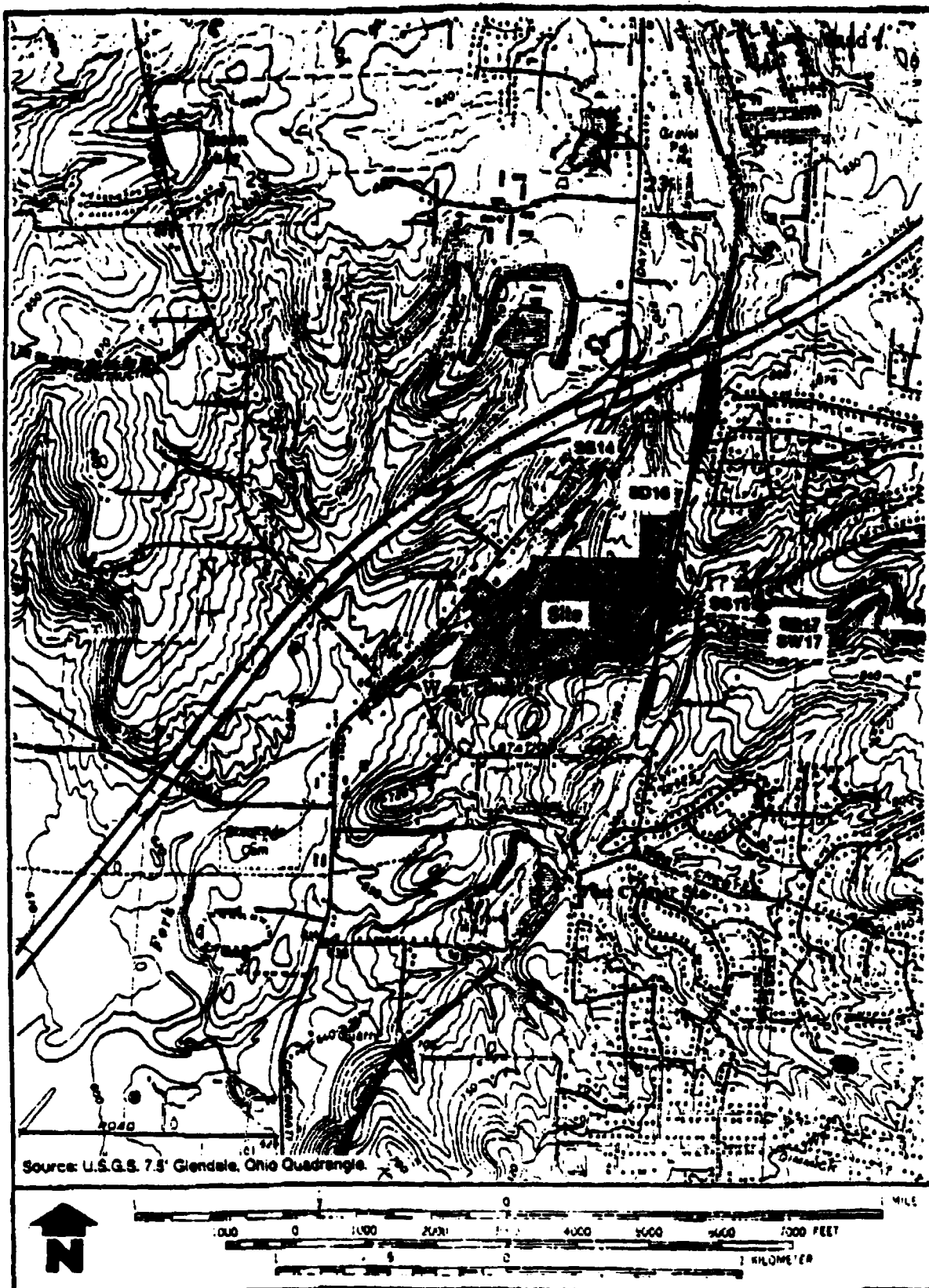
THESE ARE TRANSMITTED as checked below:

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|---|---|---|
| <input type="checkbox"/> For approval | <input type="checkbox"/> Approved as submitted | <input type="checkbox"/> Resubmit _____ copies for approval |
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REMARKS _____

COPY TO _____

SIGNED: _____



**FIGURE 1 ROUND 3 SAMPLE LOCATIONS FOR SOIL,
SEDIMENT AND SURFACE WATERS
SKINNER LANDFILL SITE**

TABLE
SUMMARY OF VOLATILE ORGANIC COMPOUND ANALYSIS
GROUNDWATER SAMPLES
SKINNER LANDFILL

	GW06-03	GW07-03	GW07-03HX	GW07-DP	GW09-03	GW10-03	GW11-03	GW12-03	GW14-03	GW15-03	GW15-BK
PHASE	3	3	3	3	3	3	3	3	3	3	3
CRL LOG NUMBER	87RA02509	87RA02510	87RA02510	87RA02510	87RA02512	87RA02513	87RA02514	87RA02515	87RA02517	87RA02518	87RA02518
TRAFFIC REPORT NUMBER	EN228	EN229	EN230	EN231	EN283	EN284	EN285	EN286	EN288	EN289	EN290
DATE COLLECTED	7/28/87	7/27/87	7/27/87	7/27/87	7/28/87	7/27/87	7/27/87	7/28/87	7/29/87	7/29/87	7/28/87
CONC/DIL FACTOR	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
UNITS	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L
1,1,1-TRICHLOROETHANE	---	---	---	---	---	---	---	---	---	---	6
1,2-DICHLOROETHANE	---	---	---	---	---	---	---	---	---	---	---
2-BUTANONE	10 J/R	10 J/R	10 J/R	10 J/R	10 J/R	10 J/R	10 J/R	10 J/R	10 J/R	10 J/R	30 J/R
2-HEXANONE	---	---	---	---	---	---	---	---	---	---	---
ACETONE	10 J	10 J	1 JB	10 J	10 J	2 J	10 J	10 J	6 J	6 J	38 J
BENZENE	---	---	---	---	---	---	---	---	---	---	---
BROMOFORM	5 J	5 J	5 J	5 J	5 J	5 J	5 J	5 J	---	---	5 J
CARBON TETRACHLORIDE	---	---	---	---	---	---	---	---	3 J	---	---
CHLOROBENZENE	---	---	---	---	---	---	2 J	2 J	---	---	1 J
CHLOROMETHANE	10 J	10 J	10 J	10 J	10 J	10 J	10 J	10 J	---	---	10 J
ETHYLBENZENE	---	---	---	---	---	---	---	---	---	---	---
METHYLENE CHLORIDE	---	---	---	---	---	---	---	---	4 J	4 J	5 J
TETRACHLOROETHENE	---	---	---	---	---	---	---	---	5 J	5 J	---
TOLUENE	---	---	---	---	---	1 J	2 J	1 J	---	1 J	5
TOTAL XYLENES	---	---	---	---	---	---	---	---	---	---	---
TRANS-1,2-DICHLOROETHENE	---	10	10	10	---	---	---	---	---	---	---

J = Material Analyzed For, But Not Detected. Estimated Quantitation Limit.
R = Data Unusable, Resampling and Reanalysis Necessary for Verification
--- = No Detection

TABLE (Cont.)
SUMMARY OF VOLATILE ORGANIC COMPOUND ANALYSIS
GROUNDWATER SAMPLES
SKINNER LANDFILL

	GW16-03	GW16-0P	GW17-03	GW18-03	GW18-0K	GW19-03	GW20-03	GW21-03	GW22-03	GW23-03
PHASE	3	3	3	3	3	3	3	3	3	3
CRL LOG NUMBER	87RA02819	87RA02819	87RA02820	87RA02821	87RA02821	87RA02822	87RA02823	87RA02824	87RA02825	87RA02826
TRAFFIC REPORT NUMBER	EN291	EN292	EN293	EN294	EN295	EN296	EN297	EN298	EN299	EN300
DATE COLLECTED	7/29/87	7/29/87	7/29/87	7/29/87	7/29/87	7/29/87	7/28/87	7/28/87	7/29/87	7/29/87
CONC/DIL FACTOR	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.10	0.50
UNITS	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L
1,1,1-TRICHLOROETHANE	1 J	---	---	---	---	---	---	---	---	---
1,2-DICHLOROETHANE	---	---	---	---	---	---	---	---	4500	---
2-BUTANONE	10 J/R	10 J/R	10 J/R	10 J/R	10 J/R	10 J/R	170 J/R	10 J/R	1000 J/R	10 J/R
2-HEXANONE	---	---	---	---	---	---	---	---	740 J	---
ACETONE	2 J	---	---	---	17	---	920	10 J	4800	---
BENZENE	---	---	---	---	---	---	400	4 J	20000	---
BROMOFORM	---	---	---	---	---	---	---	5 J	---	---
CHLOROBENZENE	3 J	2 J	---	---	---	---	26 J	8	140 J	---
CHLOROMETHANE	---	---	---	---	---	---	---	10 J	---	---
ETHYLBENZENE	---	---	---	---	---	---	52 J	---	100 J	---
METHYLENE CHLORIDE	4 J	10 J	15 J	3 J	4 J	3 J	170 J	3 J	2200 J	6 J
TETRACHLOROETHENE	5 J	---	---	---	---	---	---	---	---	---
TOLUENE	---	---	---	---	---	---	3100	2 J	530	---
TOTAL XYLENES	---	---	---	---	---	---	100	---	300 J	---
TRANS-1,2-DICHLOROETHENE	---	---	---	---	---	---	31 J	---	---	---

J = Material Analyzed For, But Not Detected. Estimated Quantitation Limit.

R = Data Unusable, Resampling and Reanalysis Necessary for Verification

--- = No Detection

TABLE
SUMMARY OF SEMI-VOLATILE ORGANIC COMPOUND ANALYSIS
GROUNDWATER SAMPLES
SKINNER LANDFILL

	GW06-03	GW07-03	GW07-03HX	GW07-DP	GW09-03	GW10-03	GW11-03	GW12-03	GW14-03	GW15-03	GW15-BK
PHASE	3	3	3	3	3	3	3	3	3	3	3
CRL LOG NUMBER	87RA02S09	87RA02S10	87RA02S10	87RA02D10	87RA02S12	87RA02S13	87RA02S14	87RA02S15	87RA02S17	87RA02S19	87RA02R1
TRAFFIC REPORT NUMBER	EN228	EN229	EN230	EN231	EN283	EN284	EN285	EN286	EN288	EN289	EN290
DATE COLLECTED	7/28/87	7/27/87	7/27/87	7/27/87	7/28/87	7/27/87	7/27/87	7/28/87	7/29/87	7/29/87	7/28/87
CONC/DIL FACTOR	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
UNITS	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L
1,4-DICHLOROBENZENE	---	---	---	---	---	---	---	---	---	---	---
2,4-DINITROPHENOL	50 J	50 J	50 J	50 J	50 J	50 J	50 J	50 J	50 J	50 J	50 J
2,4-DINITROTOLUENE	---	---	---	---	---	---	---	---	---	---	---
2-METHYLPHENOL	---	---	---	---	---	---	---	---	---	---	---
4,6-DINITRO-2-METHYLPHENOL	50 J	50 J	50 J	50 J	50 J	50 J	50 J	50 J	50 J	50 J	50 J
4-METHYLPHENOL	---	---	---	---	---	---	---	---	---	---	---
4-NITROPHENOL	---	---	---	---	---	---	---	---	---	---	---
BENZOIC ACID	50 J	50 J	50 J	50 J	---	---	50 J	50 J	---	---	50 J
BENZYL ALCOHOL	---	---	---	---	---	---	---	---	---	---	---
BIS(2-CHLOROETHYL)ETHER	---	---	---	---	---	17	---	---	---	---	---
BIS(2-ETHYLNEXYL)PHTHALATE	---	---	---	3 J	---	2 J	---	---	---	---	---
DIMETHYL PHTHALATE	---	---	---	---	---	---	---	---	---	---	---
DI-N-BUTYLPHTHALATE	---	---	---	---	---	---	---	---	---	---	---
HEXACHLOROCYCLOPENTADIENE	10 J	10 J	10 J	10 J	10 J	---	10 J	10 J	10 J	---	10 J
ISOPHRONE	---	---	---	---	---	---	---	---	---	---	---
NAPHTHALENE	---	---	---	---	---	---	---	---	---	---	---
PHENOL	---	---	---	---	---	---	---	---	---	---	---

J = Material Analyzed For, But Not Detected. Estimated Quantitation Limit.

R = Data Unusable, Resampling and Reanalysis Necessary for Verification

--- = No Detection

TABLE (Cont.)
SUMMARY OF SEMI-VOLATILE ORGANIC COMPOUND ANALYSIS
GROUNDWATER SAMPLES
SKINNER LANDFILL

	GW16-03	GW16-0P	GW17-03	GW18-03	GW18-BK	GW19-03	GW20-03	GW21-03	GW22-03	GW23-03
PHASE	3	3	3	3	3	3	3	3	3	3
CRL LOG NUMBER	87RA02S19	87RA02S19	87RA02S20	87RA02S21	87RA02S21	87RA02S22	87RA02S23	87RA02S24	87RA02S25	87RA02S26
TRAFFIC REPORT NUMBER	EN291	EN292	EN293	EN294	EN295	EN296	EN297	EN298	EN299	EN300
DATE COLLECTED	7/29/87	7/29/87	7/29/87	7/29/87	7/29/87	7/29/87	7/29/87	7/29/87	7/29/87	7/29/87
CONC/DIL FACTOR	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.10	0.50
UNITS	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L
1,4-DICHLOROBENZENE	---	---	7 J	3 J	---	---	3 J	---	---	---
2,4-DINITROPHENOL	50 J	50 J	50 J	50 J	50 J	50 J	50 J	---	---	100 J
2,4-DINITROBENZENE	---	---	---	---	---	---	---	10 J	---	---
2-METHYLPHENOL	---	---	---	---	---	---	---	---	450	---
4,6-DINITRO-2-METHYLPHENOL	50 J	50 J	50 J	50 J	50 J	50 J	50 J	50 J	500 J	100 J
4-METHYLPHENOL	---	---	---	---	---	---	---	---	350	---
4-NITROPHENOL	---	---	---	---	---	---	---	---	500 J	---
BENZOIC ACID	---	50 J	---	---	50 J	---	---	---	---	---
BENZYL ALCOHOL	---	---	---	---	---	---	9 J	---	---	---
BIS(2-CHLOROETHYL)ETHER	---	---	---	---	---	---	240	---	---	---
BIS(2-ETHYLHEXYL)PHTHALATE	---	---	---	---	---	---	---	---	---	---
DIMETHYL PHTHALATE	---	---	---	---	---	---	---	---	24 J	---
DI-N-BUTYLPHTHALATE	---	---	---	---	---	---	---	---	---	5 J
HEXACHLOROCYCLOPENTADIENE	---	10 J	---	---	10 J	10 J	---	10 J	100 J	20 J
ISOPHTHALENE	---	---	---	---	---	---	---	---	91 J	---
NAPHTHALENE	---	---	9 J	---	---	---	64	---	---	---
PHENOL	---	---	---	---	---	---	---	---	670	---

J = Material Analyzed For, But Not Detected. Estimated Quantitation Limit.

R = Data Unusable, Resampling and Reanalysis Necessary for Verification

--- = No Detection

TABLE
SUMMARY OF PESTICIDE/PCBs ORGANIC COMPOUND ANALYSIS
GROUNDWATER SAMPLES
SKINNER LANDFILL

	GW06-03	GW07-03	GW07-03HX	GW07-0P	GW09-03	GW10-03	GW11-03	GW12-03	GW14-03	GW15-03	GW15-0K
PHASE	3	3	3	3	3	3	3	3	3	3	3
CRL LOG NUMBER	87RA02S09	87RA02S10	87RA02S10	87RA02D10	87RA02S12	87RA02S13	87RA02S14	87RA02S15	87RA02S17	87RA02S19	87RA02R18
TRAFFIC REPORT NUMBER	EN228	EN229	EN230	EN231	EN283	EN284	EN285	EN286	EN288	EN289	EN290
DATE COLLECTED	7/28/87	7/27/87	7/27/87	7/27/87	7/28/87	7/27/87	7/27/87	7/28/87	7/29/87	7/29/87	7/28/87
CONC/DIL FACTOR	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
UNITS	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L
Alpha-BHC	---	---	---	---	---	---	---	---	---	---	---
Beta-BHC	---	---	---	---	---	---	---	---	---	---	---
Delta-BHC	---	---	---	---	---	---	---	---	---	---	---
Gamma-BHC	---	---	---	---	---	---	---	---	---	---	---
Heptachlor	---	---	---	---	---	---	---	---	---	---	---
Aldrin	---	---	---	---	---	---	---	---	---	---	---
Heptachlor Epoxide	---	---	---	---	---	---	---	---	---	---	---
Endosulfan I	---	---	---	---	---	---	---	---	---	---	---
Dieldrin	---	---	---	---	---	---	---	---	---	---	---
4,4-DDE	---	---	---	---	---	---	---	---	---	---	---
Endrin	---	---	---	---	---	---	---	---	---	---	---
Endosulfan II	---	---	---	---	---	---	---	---	---	---	---
4,4-DDD	---	---	---	---	---	---	---	---	---	---	---
Endrin Aldehyde	---	---	---	---	---	---	---	---	---	---	---
Endosulfan Sulfate	---	---	---	---	---	---	---	---	---	---	---
4,4-DDT	---	---	---	---	---	---	---	---	---	---	---
Methoxychlor	---	---	---	---	---	---	---	---	---	---	---
Endrin Ketone	---	---	---	---	---	---	---	---	---	---	---
Chlordane	---	---	---	---	---	---	---	---	---	---	---
Toxaphene	---	---	---	---	---	---	---	---	---	---	---
AROCLOR-1016	---	---	---	---	---	---	---	---	---	---	---
AROCLOR-1221	---	---	---	---	---	---	---	---	---	---	---
AROCLOR-1232	---	---	---	---	---	---	---	---	---	---	---
AROCLOR-1242	---	---	---	---	---	---	---	---	---	---	---
AROCLOR-1248	---	---	---	---	---	---	---	---	---	---	---
AROCLOR-1254	---	---	---	---	---	---	---	---	---	---	---
AROCLOR-1260	---	---	---	---	---	---	---	---	---	---	---

--- = No Detection

TABLE (Cont.)
SUMMARY OF PESTICIDE/PCBs ORGANIC COMPOUND ANALYSIS
GROUNDWATER SAMPLES
SKINNER LANDFILL

	GW16-03	GW16-0P	GW17-03	GW18-03	GW18-0K	GW19-03	GW20-03	GW21-03	GW22-03	GW23-03
PHASE	3	3	3	3	3	3	3	3	3	3
CRL LOG NUMBER	87RA02519	87RA02519	87RA02520	87RA02521	87RA02521	87RA02522	87RA02523	87RA02524	87RA02525	87RA02526
TRAFFIC REPORT NUMBER	EN291	EN292	EN293	EN294	EN295	EN296	EN297	EN298	EN299	EN300
DATE COLLECTED	7/29/87	7/29/87	7/29/87	7/29/87	7/29/87	7/29/87	7/28/87	7/28/87	7/29/87	7/29/87
CONC/DIL FACTOR	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.10	0.50
UNITS	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L
Alpha-BHC	---	---	---	---	---	---	---	---	---	---
Beta-BHC	---	---	---	---	---	---	---	---	---	---
Delta-BHC	---	---	---	---	---	---	---	---	---	---
Gamma-BHC	---	---	---	---	---	---	---	---	---	---
Heptachlor	---	---	---	---	---	---	---	---	---	---
Aldrin	---	---	---	---	---	---	---	---	---	---
Heptachlor Epoxide	---	---	---	---	---	---	---	---	---	---
Endosulfan I	---	---	---	---	---	---	---	---	---	---
Dieldrin	---	---	---	---	---	---	---	---	---	---
4,4-DDE	---	---	---	---	---	---	---	---	---	---
Endrin	---	---	---	---	---	---	---	---	---	---
Endosulfan II	---	---	---	---	---	---	---	---	---	---
4,4-DDD	---	---	---	---	---	---	---	---	---	---
Endrin Aldehyde	---	---	---	---	---	---	---	---	---	---
Endosulfan Sulfate	---	---	---	---	---	---	---	---	---	---
4,4-DDT	---	---	---	---	---	---	---	---	---	---
Methoxychlor	---	---	---	---	---	---	---	---	---	---
Endrin Ketone	---	---	---	---	---	---	---	---	---	---
Chlordane	---	---	---	---	---	---	---	---	---	---
Toxaphene	---	---	---	---	---	---	---	---	---	---
AROCLOR-1016	---	---	---	---	---	---	---	---	---	---
AROCLOR-1221	---	---	---	---	---	---	---	---	---	---
AROCLOR-1232	---	---	---	---	---	---	---	---	---	---
AROCLOR-1242	---	---	---	---	---	---	---	---	---	---
AROCLOR-1248	---	---	---	---	---	---	---	---	---	---
AROCLOR-1254	---	---	---	---	---	---	---	---	---	---
AROCLOR-1260	---	---	---	---	---	---	---	---	---	---

--- = No Detection

TABLE
SUMMARY OF SAS PESTICIDE/PCBs ORGANIC COMPOUND ANALYSIS
GROUNDWATER SAMPLES
SKINNER LANDFILL

	GW06-03	GW07-03	GW07-03HX	GW09-03	GW10-03	GW11-03	GW12-03	GW14-03	GW15-03	GW15-BK
PHASE	3	3	3	3	3	3	3	3	3	3
CRL LOG NUMBER	87RA02S09	87RA02S10	87RA02S10	87RA02S12	87RA02S13	87RA02S14	87RA02S15	87RA02S17	87RA02S18	87RA02R18
TRAFFIC REPORT NUMBER	EN228	EN229	EN230	EN283	EN284	EN285	EN286	EN288	EN289	EN290
DATE COLLECTED	7/28/87	7/27/87	7/27/87	7/28/87	7/27/87	7/27/87	7/28/87	7/29/87	7/29/87	7/28/87
CONC/DIL FACTOR	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
UNITS	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L
Hexachlorobenzene	---	---	---	---	---	---	---	---	---	---
Hexachlorocyclopentadiene	---	---	---	---	---	---	---	---	---	---
Hexachlorobutadiene	---	---	---	---	---	---	---	---	---	---
Hexachloronorbornadiene	---	---	---	---	---	---	---	---	---	---
Octachlorocyclopentene	---	---	---	---	---	---	---	---	---	---
Heptachloronorbornene	---	---	---	---	---	---	---	---	---	---
Alpha-Chlordene	---	---	---	---	---	---	---	---	---	---
Beta-Chlordene	---	---	---	---	---	---	---	---	---	---
Gamma-Chlordene	---	---	---	---	---	---	---	---	---	---

--- = Not Detected

TABLE (Cont.)
SUMMARY OF SAS PESTICIDE/PCBs ORGANIC COMPOUND ANALYSIS
GROUNDWATER SAMPLES
SKINNER LANDFILL

	GW16-03	GW16-DP	GW17-03	GW18-03	GW18-BK	GW19-03	GW20-03	GW21-03	GW22-03
PHASE	3	3	3	3	3	3	3	3	3
CRL LOG NUMBER	87RA02s19	87RA02s19	87RA02s20	87RA02s21	87RA02s21	87RA02s22	87RA02s23	87RA02s24	87RA02s25
TRAFFIC REPORT NUMBER	EN291	EN292	EN293	EN294	EN295	EN296	EN297	EN298	EN299
DATE COLLECTED	7/29/87	7/29/87	7/29/87	7/29/87	7/29/87	7/29/87	7/28/87	7/28/87	7/29/87
CONC/DIL FACTOR	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.10
UNITS	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L
Hexachlorobenzene	---	---	---	---	---	---	---	---	---
Hexachlorocyclopentadiene	---	---	---	---	---	---	---	---	---
Hexachlorobutadiene	---	---	---	---	---	---	---	---	---
Hexachloronorborene	---	---	---	---	---	---	---	---	---
Octachlorocyclopentene	---	---	---	---	---	---	---	---	---
Heptachloronorborene	---	---	---	---	---	---	---	---	---
Alpha-Chlordane	---	---	---	---	---	---	---	---	---
Beta-Chlordane	---	---	---	---	---	---	---	---	---
Gamma-Chlordane	---	---	---	---	---	---	---	---	---

--- = Not Detected

TABLE
SUMMARY OF INORGANIC AND CYANIDE COMPOUND ANALYSIS
GROUNDWATER AND SURFACE WATER SAMPLES
SKINNER LANDFILL

	GW07-03	GW07-09	GW12-03	GW15-03	GW15-BK	GW20-03	SW17-01
PHASE	3	3	3	3	3	3	3
CRL LOG NUMBER	87RA02S10	87RA02D10	87RA02S15	87RA02S18	87RA02R18	87RA02S23	87RA02S08
TRAFFIC REPORT NUMBER	MEM037	MEM039	MEM040	MEM041	MEM042	MEM043	MEM038
DATE COLLECTED	7/27/87	7/27/87	7/28/87	7/29/87	7/28/87	7/28/87	7/29/87
CONC/DIL FACTOR	1.00	1.00	1.00	1.00	1.00	1.00	1.00
UNITS	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L	UG/L
Aluminum	96 J	23 J	20 J	---	19 J	---	502
Antimony	---	---	---	---	---	---	---
Arsenic	---	---	---	---	---	48	---
Barium	101 J	97 J	73 J	85 J	---	597	46 J
Beryllium	---	---	---	---	---	---	---
Cadmium	---	---	---	---	---	---	---
Calcium	13600	133000	239000	164000	232 J	195000	69200
Chromium	---	---	---	---	---	---	---
Cobalt	---	---	9.3 J	---	---	---	---
Copper	6.2 J	8.3 J	10 J	6.9 J	---	---	7 J
Iron	49 J	---	35 J	26 J	---	31600	872
Lead	---	---	---	---	---	---	---
Magnesium	22000	20900	83100	33800	---	51600	20100
Manganese	484	466	3490	2280	---	1150	35
Mercury	---	---	---	---	---	---	---
Nickel	---	---	38 J	8.7 J	---	20 J	---
Potassium	1610 J	1330	34700	8410	---	41500	3920 J
Selenium	---	---	---	---	---	---	---
Silver	---	---	---	---	---	---	---
Sodium	29600	30000	158000	76400	---	81200	19400
Thallium	---	---	---	---	---	---	---
Tin	---	---	---	---	---	---	---
Vanadium	---	---	---	---	---	---	---
Zinc	25	22	10 J	5.4 J	3.9 J	12 J	7.2 J
Cyanide	---	---	---	---	---	---	---

J = Estimated Value

--- = Not Detected

GW = Groundwater

SW = Surface Water

TABLE
SUMMARY OF VOLATILE ORGANIC COMPOUND ANALYSIS
SOIL AND SURFACE WATER SAMPLES
SKINNER LANDFILL

	SS14-01	SS14-0P	SS14-02	SS15-01	SS15-01	SS15-02	SD16-01	SD17-01	SU17-01
PHASE	3	3	3	3	3	3	3	3	3
CRL LOG NUMBER	87RA02901	87RA02901	87RA02902	87RA02903	87RA02903	87RA02904	87RA02905	87RA02906	87RA02908
TRAFFIC REPORT NUMBER	EN077	EN078	EN079	EN080	EN081	EN223	EN224	EN225	EN227
DATE COLLECTED	7/29/87	7/29/87	7/29/87	7/29/87	7/29/87	7/29/87	7/29/87	7/29/87	7/29/87
CONC/DIL FACTOR	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
UNITS	UG/KG	UG/KG	UG/KG	UG/KG	UG/KG	UG/KG	UG/KG	UG/KG	UG/KG
CHLOROMETHANE	12 J	12 J	12 J	14 J	14 J	13 J	13 J	11 J	---
METHYLENE CHLORIDE	4 J	5 J	7 J	6 J	5 J	7 J	9 J	7 J	5 J
2-BUTANONE	12 J/R	12 J/R	12 J/R	14 J/R	14 J/R	13 J/R	13 J/R	11 J/R	10 J/R
1,1,1-TRICHLOROETHANE	23	9	---	25	24	---	10	---	---
4-METHYL-2-PENTANONE	12 J	12 J	---	14 J	14 J	---	---	---	---
TOLUENE	17	12	39	---	---	3 J	---	---	---
TETRACHLOROETHENE	---	---	---	---	---	---	---	---	5 J
ACETONE	---	---	---	---	---	---	---	---	4 J

J = Material Analyzed For, But Not Detected. Estimated Quantitation Limit.
R = Data Unusable, Resampling and Reanalysis Necessary for Verification
--- = No Detection
SS = Surface Soil
SD = Sediment
SU = Surface Water

TABLE
SUMMARY OF SEMI-VOLATILE ORGANIC COMPOUND ANALYSIS
SOIL AND SURFACE WATER SAMPLES
SKINNER LANDFILL

	SS14-01	SS14-DP	SS14-02	SS15-01	SS15-01	SS15-02	SD16-01	SD17-01	SW17-01
PHASE	3	3	3	3	3	3	3	3	3
CRL LOG NUMBER	87RA02S01	87RA02D01	87RA02S02	87RA02S03	87RA02S03	87RA02S04	87RA02S05	87RA02S06	87RA02S08
TRAFFIC REPORT NUMBER	EN077	EN078	EN079	EN080	EN081	EN223	EN224	EN225	EN227
DATE COLLECTED	7/29/87	7/29/87	7/29/87	7/29/87	7/29/87	7/29/87	7/29/87	7/29/87	7/29/87
CONC/DIL FACTOR	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
UNITS	UG/KG	UG/KG	UG/KG	UG/KG	UG/KG	UG/KG	UG/KG	UG/KG	UG/KG
BENZOIC ACID	2900 J	3000 J	2900 J	3400 J	3400 J	3000 J	3200 J	2700 J	---
HEXACHLOROCYCLOPENTADIENE	590 J	620 J	590 J	710 J	690 J	620 J	660 J	560 J	10 J
2-NITROANILINE	2900 J	3000 J	2900 J	3400 J	3400 J	3000 J	3200 J	2700 J	---
BUTYLBENZYLPHthalATE	73 J	620 J	590 J	710 J	690 J	620 J	660 J	560 J	---
BIS(2-ETHYLHEXYL)PHTHALATE	590 J	620 J	590 J	200 J	690 J	620 J	660 J	560 J	---
INDENO(1,2,3-CD)PYRENE	590 J	620 J	590 J	710 J	690 J	620 J	660 J	560 J	---
DIBENZ(a,h)ANTHRACENE	590 J	620 J	590 J	710 J	690 J	620 J	660 J	560 J	---
BENZO(g,h,i)PERYLENE	590 J	620 J	590 J	710 J	690 J	620 J	660 J	560 J	---
2,4-DINITROPHENOL	---	---	---	---	---	---	---	---	50 J
4,6-DINITRO-2-METHYLPHENOL	---	---	---	---	---	---	---	---	50 J

J = Material Analyzed For, But Not Detected. Estimated Quantitation Limit.

R = Data Unusable, Resampling and Reanalysis Necessary for Verification

--- = No Detection

SS = Surface Soil

SD = Sediment

SW = Surface Water

TABLE
SUMMARY OF PESTICIDE/PCBs ORGANIC COMPOUND ANALYSIS
SOIL AND SURFACE WATER SAMPLES
SKINNER LANDFILL

	SS14-01	SS14-0P	SS14-02	SS15-01	SS15-01	SS15-02	SD16-01	SD17-01	SW17-01
PHASE	3	3	3	3	3	3	3	3	3
CRL LOG NUMBER	87RA02501	87RA02501	87RA02502	87RA02503	87RA02503	87RA02504	87RA02505	87RA02506	87RA02508
TRAFFIC REPORT NUMBER	EN077	EN078	EN079	EN080	EN081	EN223	EN224	EN225	EN227
DATE COLLECTED	7/29/87	7/29/87	7/29/87	7/29/87	7/29/87	7/29/87	7/29/87	7/29/87	7/29/87
CONC/DIL FACTOR	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
UNITS	UG/KG	UG/KG	UG/KG	UG/KG	UG/KG	UG/KG	UG/KG	UG/KG	UG/KG
Alpha-BHC	---	---	---	---	---	---	---	---	---
Beta-BHC	---	---	---	---	---	---	---	---	---
Delta-BHC	---	---	---	---	---	---	---	---	---
Gamma-BHC	---	---	---	---	---	---	---	---	---
Heptachlor	---	---	---	---	---	---	---	---	---
Aldrin	---	---	---	---	---	---	---	---	---
Heptachlor Epoxide	---	---	---	---	---	---	---	---	---
Endosulfan I	---	---	---	---	---	---	---	---	---
Dieldrin	---	---	---	---	---	---	---	---	---
4,4-DDE	---	---	---	---	---	---	---	---	---
Endrin	---	---	---	---	---	---	---	---	---
Endosulfan II	---	---	---	---	---	---	---	---	---
4,4-DDD	---	---	---	---	---	---	---	---	---
Endrin Aldehyde	---	---	---	---	---	---	---	---	---
Endosulfan Sulfate	---	---	---	---	---	---	---	---	---
4,4-DDT	---	---	---	---	---	---	---	---	---
Methoxychlor	---	---	---	---	---	---	---	---	---
Endrin Ketone	---	---	---	---	---	---	---	---	---
Chlordane	---	---	---	---	---	---	---	---	---
Toxaphene	---	---	---	---	---	---	---	---	---
AROCLOR-1016	---	---	---	---	---	---	---	---	---
AROCLOR-1221	---	---	---	---	---	---	---	---	---
AROCLOR-1232	---	---	---	---	---	---	---	---	---
AROCLOR-1242	---	---	---	---	---	---	---	---	---
AROCLOR-1248	---	---	---	---	---	---	---	---	---
AROCLOR-1254	---	---	---	---	---	---	---	---	---
AROCLOR-1260	---	---	---	---	---	---	---	---	---

--- = " Detection
SS = face Soil

SD = Sediment
SW = Surface Water

TABLE
SUMMARY OF SAS PESTICIDE/PCBs ORGANIC COMPOUND ANALYSIS
SOIL AND SURFACE WATER SAMPLES
SKINNER LANDFILL

	SS14-01	SS14-0P	SS14-02	SS15-01	SS15-01	SS15-02	SD16-01	SD17-01	SW17-01
PHASE	3	3	3	3	3	3	3	3	3
CRL LOG NUMBER	87RA02S01	87RA02S01	87RA02S02	87RA02S03	87RA02S03	87RA02S04	87RA02S05	87RA02S06	87RA02S08
TRAFFIC REPORT NUMBER	EN077	EN078	EN079	EN080	EN081	EN223	EN224	EN225	EN227
DATE COLLECTED	7/29/87	7/29/87	7/29/87	7/29/87	7/29/87	7/29/87	7/29/87	7/29/87	7/29/87
CONC/DIL FACTOR	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
UNITS	UG/KG	UG/KG	UG/KG	UG/KG	UG/KG	UG/KG	UG/KG	UG/KG	UG/KG
Hexachlorobenzene	---	---	---	---	---	---	---	---	---
Hexachlorocyclopentadiene	---	---	---	---	---	---	---	---	---
Hexachlorobutadiene	---	---	---	---	---	---	---	---	---
Hexachloronorborene	---	---	---	---	---	---	---	---	---
Octachlorocyclopentene	---	---	---	---	---	---	---	---	---
Heptachloronorborene	---	---	---	---	---	---	---	---	---
Alpha-Chlordene	---	---	---	---	---	---	---	---	---
Beta-Chlordene	---	---	---	---	---	---	---	---	---
Gamma-Chlordene	---	---	---	---	---	---	---	---	---

--- = No Detection
SS = Surface Soil
SD = Sediment
SW = Surface Water

TABLE
SUMMARY OF INORGANIC AND CYANIDE COMPOUND ANALYSIS
SEDIMENT SAMPLES
SKINNER LANDFILL

	SS14-01	SS14-02	SS14-0P	SS15-01	SS15-01	SS15-02	SD16-01	SD17-01
PHASE	3	3	3	3	3	3	3	3
CRL LOG NUMBER	87RA02601	87RA02602	87RA02601	87RA02603	87RA02603	87RA02604	87RA02605	87RA02606
TRAFFIC REPORT NUMBER	MEW792	MEW794	MEW793	MEW795	MEW796	MEW797	MEW798	MEW799
DATE COLLECTED	7/29/87	7/29/87	7/29/87	7/29/87	7/29/87	7/29/87	7/29/87	7/29/87
CONC/DIL FACTOR	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
UNITS	MG/KG	MG/KG	MG/KG	MG/KG	MG/KG	MG/KG	MG/KG	MG/KG
Aluminum	9320	11700	9350	9790	10400	9510	8070	5960
Antimony	---	---	---	---	---	---	---	---
Arsenic	6.8	11	8.8	8.1	9.3	8	8.8	9
Barium	111 J	116	101 J	101 J	106 J	172	93 J	327
Beryllium	0.83 J	0.94 J	0.84 J	0.8 J	---	0.87	---	0.65 J
Cadmium	---	---	---	---	---	---	---	---
Calcium	15200	15500	13900	27400	23300	36900	41600	109000
Chromium	15	17	14	15	16	14	13	10
Cobalt	8.6 J	12 J	9.8 J	9.8 J	9.2 J	12 J	11 J	10 J
Copper	17	19	17	24	22	18	19	14
Iron	23100	25700	21500	23800	24800	24300	21500	23900
Lead	25	18	29	39	42	27	32	13
Magnesium	2790 J	3300	2830	3890	3740	3170	6040	14900
Manganese	1420	1390	1280	1630	1670	2570	1810	3310
Mercury	---	---	0.14	---	0.23	---	---	10
Nickel	21 J	25	22 J	22 J	23 J	24 J	22 J	26
Potassium	1020 J	1170 J	1100 J	1820	1720 J	1460 J	1090 J	740 J
Selenium	---	---	---	---	---	---	---	---
Silver	---	---	---	---	---	---	---	---
Sodium	29600	698 J	---	---	---	---	---	---
Thallium	---	---	---	---	---	---	---	---
Tin	---	---	---	---	---	---	---	---
Vanadium	22 J	26 J	21 J	24 J	24 J	24 J	20 J	23 J
Zinc	65	65	69	90	89	63	109	52
Cyanide	---	---	---	---	---	---	---	---
Percent Solids	85	87	84	74	73	81	74	90

J = Field Value
--- = Detected

SS = Surface Soil
SD = Sediment

SW = Surface Water

SOIL GAS SURVEY

REM II REMEDIAL RESPONSE TEAM

TO: Mr. Gene Wong		DATE: 5/12/87
		SITE NAME: Skinner
		SITE NUMBER: 130
FROM: AM Bort		DOCUMENT CONTROL NO.
THE FOLLOWING DOCUMENT(S) ARE TRANSMITTED:		
<div style="display: flex; justify-content: space-between;"> <input checked="" type="checkbox"/> HEREWITH <input type="checkbox"/> UNDER SEPARATE COVER </div> <div style="display: flex; justify-content: space-between;"> <input type="checkbox"/> BY MESSENGER <input type="checkbox"/> OTHER() </div>		
TITLE	NO. OF COPIES	CIRCULATION
DRAFT Soil gas survey Tech memo	1	
THE DOCUMENTS CAN BE CLASSIFIED AS THE FOLLOWING: <div style="display: flex; flex-wrap: wrap; justify-content: space-around; margin-top: 10px;"> <div style="width: 45%; text-align: center;"> <input type="checkbox"/> APPROVED </div> <div style="width: 45%; text-align: center;"> <input type="checkbox"/> RETURNED FOR CORRECTION AND RESUBMITTAL </div> <div style="width: 45%; text-align: center;"> <input type="checkbox"/> APPROVED AS NOTED </div> <div style="width: 45%; text-align: center;"> <input checked="" type="checkbox"/> PER YOUR REQUEST </div> <div style="width: 45%; text-align: center;"> <input checked="" type="checkbox"/> FOR YOUR INFORMATION </div> <div style="width: 45%; text-align: center;"> <input type="checkbox"/> CLASSIFIED CONFIDENTIAL </div> <div style="width: 45%; text-align: center;"> <input type="checkbox"/> OTHER: _____ </div> </div>		
NOTE: The figure 7 has not been finalized as yet. We will wait for your input		
THE LISTED DOCUMENTS ARE TO BE RETURNED TO: _____ ON THE FOLLOWING DATE: _____		

DRAFT

SOIL GAS SURVEY

Purpose and Scope

A soil gas survey was conducted at the Skinner Landfill site from April 6 to April 10, 1987. The initial purpose of the soil gas survey was to expand on the previously conducted geophysical survey by exploring locations with anomalous readings in the central shoulder area that were possible buried drum nests. Further, the buried lagoon area was to be surveyed to determine the areas of highest contaminant concentration. The results of the soil gas survey were then to be correlated with the geophysical results to develop a soil boring program to further characterize the areas of potential contamination.

The initial scope of work called for the installation of approximately 150 soil probes in the study area which consisted of the central shoulder and buried lagoon areas of the site. The probes were to be placed in predetermined locations on the existing site grid system utilized for the geophysical survey. In this manner, the two surveys could be correlated to achieve the stated purpose.

Theory

The instrument used for the soil gas survey was the Miran 1B Portable Ambient Air Analyzer. The Miran 1B is a microprocessor-controlled instrument that can detect and quantitatively measure over 100 compounds at concentrations from a few ppb to the percent range. The instrument is a portable ambient air analyzer that can be used to quantitatively measure to within ± 5 ppm a wide variety of organic vapors. The concentration of organic vapors present is measured by using the principle of infrared absorption. The principle of operation, as stated in the operating manual, is:

Infrared energy is emitted from a nichrome wire source through a light pipe assembly. The light is then directed to the filter wheel that allows energy at the selected wave-length to pass through into the gas cell. The sample is drawn into the cell by the integral air pump at a rate of 25 to 30 litres per minute. The sample absorbs infrared energy from the beam, and the amount of absorption is measured by the detector, amplified and converted to concentration units by the electronics, and transmitted to the liquid crystal display. The amount of infrared radiation absorbed by a sample is directly related to the concentration of the sample according to Beer's Law:

$$A = a \times b \times c$$

where A is absorbance, a is the absorbtivity constant, b is the pathlength, and c is the concentration. The MIRAN 1B also incorporates a curve correction term to correct for any deviations from Beer's Law.

Three compounds were chosen for the soil gas survey based on frequency of occurrence and concentration determined from the Phase 1 analytical results. These compounds included benzene, methylene chloride and toluene. Because the Miran 1B tests for one compound at a time to calculate a specific concentration, there is little chance for any type of interference. Interference could occur in the analysis of two compounds with absorption wavelengths within 0.5 microns. The wavelengths for benzene, methylene chloride, and toluene are 9.93, 13.47, and 13.89 microns, respectively. There would be no interference effects from toluene and methylene chloride in the measurement of benzene. The possibility for interference between methylene chloride and benzene does exist, however, based on the results, there does not appear to have been interference. This is discussed further in the Survey Results section. Other compounds with wavelengths within 0.5 microns of the compounds being analyzed could also interfere with the results. Compounds with wavelengths within 0.5 microns of benzene, methylene chloride, or toluene that could be present at the Skinner Landfill site are given in Table 1.

The instrument takes readings continuously (once every 2 seconds) and for this survey, readings were recorded once every 30 seconds. The absorption wavelengths of three compounds measured in this survey are included in the pre-programmed library of the instrument. Therefore, no precalibration for this study was needed.

Field Program

Upon arrival at the site, it was discovered that the majority of the proposed study area had been covered with 5 to 20 feet of demolition debris and solid waste. The fill had covered both the existing site grid system and the proposed soil probe locations. This necessitated a revision in the anticipated scope of work.

The southern-most portion of the central shoulder and buried lagoon areas were covered with fill to a maximum thickness of approximately 10 feet. It was decided by the U.S. EPA RPM and the WESTON Site Manager to conduct the soil gas survey in this area. A grid system to locate the soil probes was constructed utilizing existing monitoring wells on site. The location of this grid system is shown in Figure 1.

A total of 19 soil probes were placed within the grid system and the locations are shown in Figure 2.

The soil probes were 5 feet long and 1/2 inch in diameter with 3-inch pointed tips. The bottom one foot of each probe was slotted to allow air entry. The top of each probe had a threaded cap. Figure 3 contains a schematic diagram of the probes.

Because the probes had to be placed in the soil below the recent fill to accurately assess the amount of contamination present, 5-foot extenders with threaded ends were constructed to increase the length of the probes. When the extenders, which also had threaded caps, were attached, the probes were long enough to penetrate the soil below the recent fill.

TABLE 1

POSSIBLE INTERFERENCE COMPOUNDS PRESENT
AT THE SKINNER LANDFILL SITE

<u>Compound</u>	<u>Wavelength</u>
m-dichlorobenzene	9.47
o-dichlorobenzene	13.55
p-dichlorobenzene	9.30
ethylbenzene	9.90
xylene	13.20

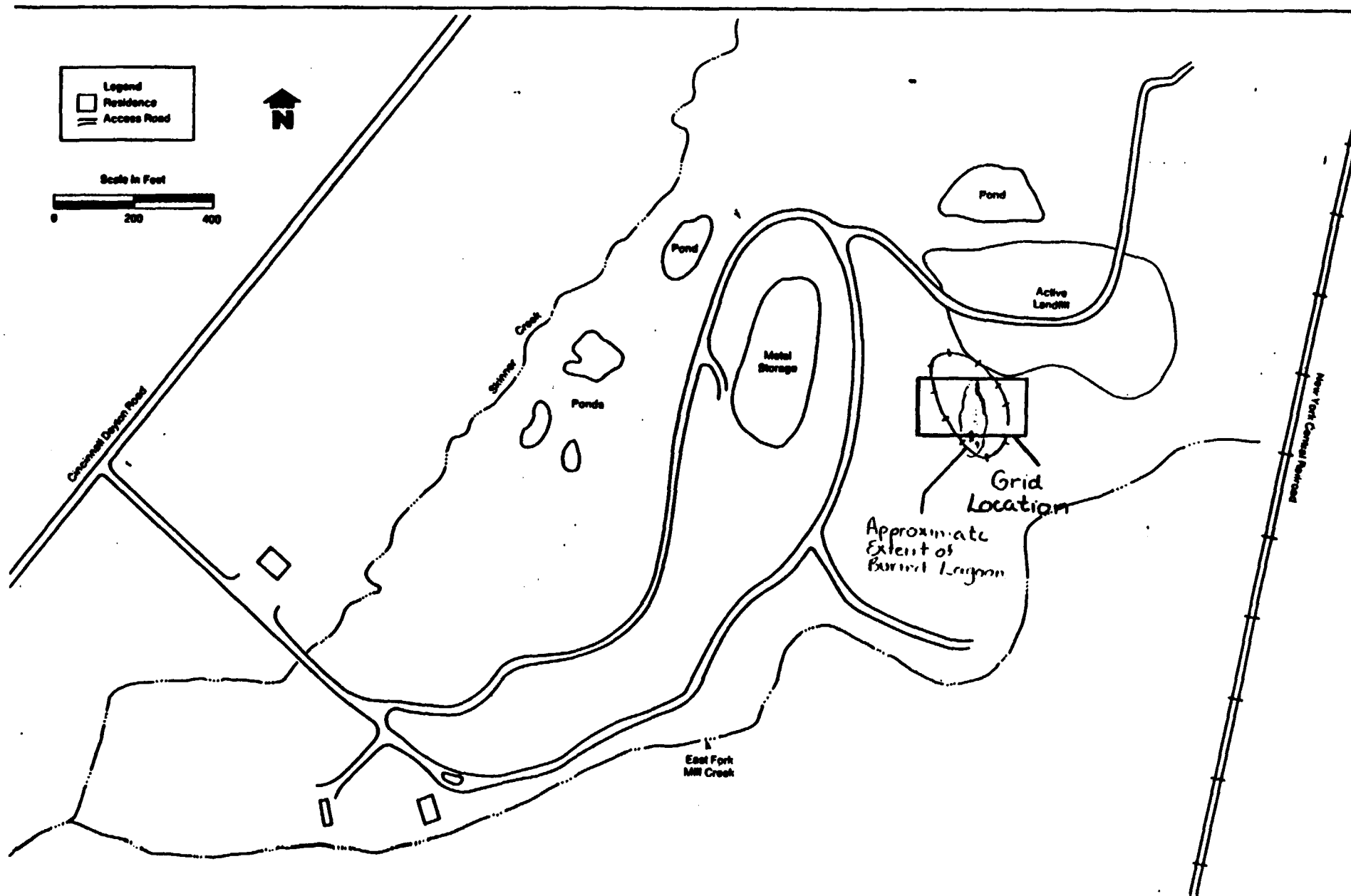


FIGURE LOCATION OF SOIL SURVEY GRID ON SITE.

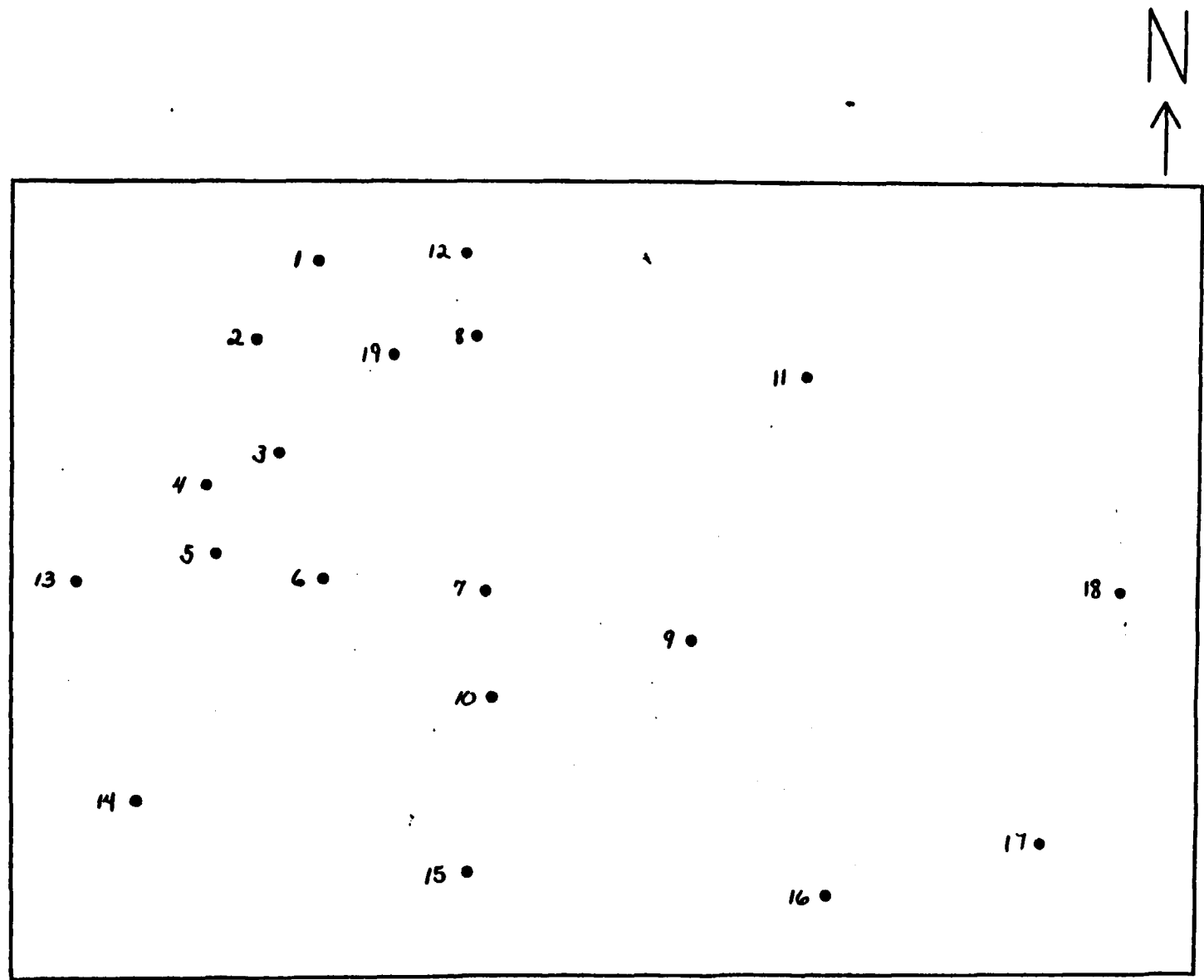


FIGURE SOIL PROBE LOCATIONS.

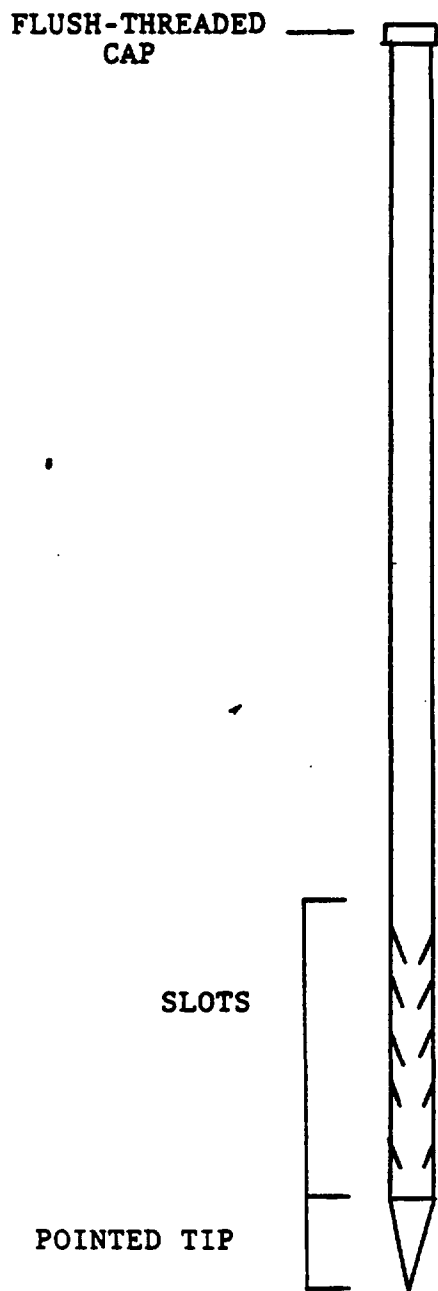


FIGURE DIAGRAM OF SOIL PROBE USED AT THE SKINNER LANDFILL SITE.

Prior to installation, each probe and extender was washed with a water and Alconox solution and rinsed first with methonal and then de-ionized water. After placement to a depth of approximately 9.5 feet, the probes were capped and allowed to stabilize for 24 hours. Before use each day, the instrument was taken off site to obtain a background concentration for the compound being analyzed. The ambient air concentration of the compound being measured was also recorded at each probe location prior to attachment to the probe.

Tygon tubing was attached to the instrument, the probe was uncapped, and the tubing was attached to the probe. Then, measurements of the concentrations were recorded once every 30 seconds until readings stabilized. Stabilization usually occurred within four to five minutes. Table 2 summarizes these results for each compound. The measurements for methylene chloride were obtained at all probes first. The probe was then recalibrated to background and measurements for benzene were taken. Toluene was the third compound tested for at the probes.

Discussion of Results

The stabilized results of the soil gas readings are plotted on the maps in Figures 3, 4, and 5. Concentrations of methylene chloride ranged from 2.2 to 868 ppm, benzene from 1.2 to 50 ppm, and toluene from 1.7 to 768 ppm. There does not appear to be any trend to the data, rather there appears to be a series of "hot spots" where one or more of the compounds was detected at high concentrations.

Because the range of concentrations of methylene chloride were 10 to 30 times higher than the concentrations of benzene, there appears to be no interference (discussed in the "Theory" section) between the two compounds. The interference usually occurs at concentrations less than 10 ppm, therefore, the concentrations are most likely accurate. Also based on the consistency of results, the higher (>10 ppm) concentrations of most readings, and the accuracy of the instrument, the readings are probably correct to within ± 5 ppm.

The areas of highest concentration of one or more compounds occur in the northwest and west portion of the survey area, in the area of the buried lagoon, and there are also some scattered "hot spots" in the north-central and central areas of the survey.

The results of the soil gas survey were correlated to the results of the geophysical survey conducted previously by overlaying the two grid systems. This correlation indicated that several areas of contamination are indicated by both surveys. Probes 1, 2, 3, and 8 are located in one area of high conductivity and Probes 7, 9 and 10 are in another, as indicated by the EM survey. Probes 8 and 9 are also located in areas that were determined to be possible drum nests by the GPR survey.

By utilizing these correlated results, the proposed test trench locations, to further characterize the contamination present are presented in Figure 7.

TABLE 2
SKINNER LANDFILL SOIL GAS PROBE DATA
METHYLENE CHLORIDE (in ppm)

PROBE:	1D	1D DUP	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
INITIAL TIME:	8:35	12:24	8:44	8:53	9:00	9:05	9:11	9:19	9:31	9:39	9:51	9:58	10:09	10:18	10:31	10:40	11:38	11:45	11:52	12:02
BACKGROUND:	10	-0.5	14	18	14	15	11	13	12	18	15	15	14	19	19	20	0.2	-3	-2.1	-0.5
TIME (min)																				
0.0	10	-0.5	14	18	14	15	12	13	10	140	15	15	14	20	19	20	0.2	-3	-2.1	-0.5
0.5	464	220	12	19	27	9.2	93	33	208	188	115	64	74	22	351		21	-4	8.4	2.4
1.0	620	527	9.4		39					214	169	84	139		480	23	34	-1	9.4	2.2
1.5	623	663	8.4	18	42	9.5	133	152	382	219	186	87	160	240	508	24	39	-0.8	8.1	0
2.0	623	739	5.1	18	42	13	144	229	413	228	191	90	168	353	524	45	44	-0.2	7.5	
2.5	642	784	8.4	17	42	12	148	257	432	231	192	91	172	368	531	65	49			
3.0	652	817	8.3	19	41	12	152	266	445	234	194	92	172	550	534	84	49			
3.5	656	838					154	272	454	238	195	92	173	617	537	100				
4.0	657	841					155	274	462	241	194		175	692	538	120				
4.5	658	845					156	275	464	242			175	715	538	138				
5.0							155	274	463	243			174	754		150				
5.5										242				788		161				
6.0														801		170				
6.5														823		179				
7.0														841		188				
7.5														854		194				
8.0														868		200				
8.5																207				
9.0																211				

NOTES

INITIAL TIME indicates time analysis of gas from probe commenced.
 All analysis for methylene chloride were completed on 04/08/87.
 D indicates deep soil gas probe.
 DUP indicates duplicate sampling and analysis.

TABLE 2 (con't)
SKINNER LANDFILL SOIL GAS PROBE DATA
TOLUENE (in ppm)

PROBE:	10	15	20	25	30	35	4	50	55	6	7	8	9	10	11	135
INITIAL TIME:	10:51	11:03	11:20	11:32	11:37	11:41	12:05	11:46	11:48	12:10	12:14	11:09	12:19	12:24	12:29	11:54
BACKGROUND:	0	2.5	1.2	1.4	2.2	16	1.5	2.5	3	2.9	0.4	1.3	4.5	4	2.5	0.9
TIME (min)																
0.0	-0.2	2.5	1.2	1.4	2.2	16	1.5	2.5	3	2.9	0.4	1.3	4.5	4	2.5	0.9
0.5	1.6	94	0.2	343	1.1	650	41	2.7	40	97	130	222	140	98	38	2.8
1.0	105	127	0.7	517	1.1	755	46	3.2	51	128	168	310	189	122	46	89
1.5	179	140	1	542	0.7	765	49	4.3	56	140	179	339	203	133	52	211
2.0	253	145	0.9	569	1.2	768	47	3.4	59	146	186	354	212	139	54	277
2.5	306	148	1	570	0.8	769	47		61	149	188	361	216	141	55	330
3.0	348	148	1.7	568		768			61	149	189	361	218	141	54	401
3.5	385	149										366	221	141	52	451
4.0	410											367	218		50	497
4.5	433														49	537
5.0	451															567
5.5	467															594
6.0	481															617
6.5	492															640
7.0	500															658
7.5	506															673
8.0	515															687
8.5	519															695
9.0	524															704
9.5	527															715
10.0	531															725
10.5	534															

NOTES

INITIAL TIME indicates time analysis of soil gas using probe commenced.
All analysis for toluene were completed on 04/09/87.

TABLE 2 (con't)
SKINNER LANDFILL SOIL GAS PROBE DATA
BENZENE (in ppb)

PROBE:	10	18	20	28	30	38	4	50	58	6	7	8	9	10 CF	10 PF	11	190	195
INITIAL TIME:	8:41	8:51	8:57	9:02	9:08	9:13	9:18	9:43	9:50	9:55	10:00	9:23	10:06	10:12	10:18	10:24	9:31	9:35
BACKGROUND:	4.5	-0.5	-0.3	-1.5	0.8	1.2	3.1	3.5	5.1	5.2	6.8	1.1	5.2	4.9	4.9	4.2	3.3	2.4
TIME (min)																		
0.0	2.4	-0.5	-0.3	-1.5	0.8	1.2	3.1	3.5	5.1	5.2	6.8	1.1	5.2	4.9	5	4.2	3.3	2.4
0.5	-0.9	1.5	0.1	17	3.2	24	6.3	5.1	7.5	7.4	12	8.2	9.5	9.3	12	9.3	5.5	9.6
1.0	-0.6	5.6	0.2	26	3.3	34	9.7	6.7	11	13	16	13	12	11	14	12	7.9	19
1.5	0.9	7	0.3	29	3.3	40	10	8.6	11	15	17	18	14	13	15	12	8.6	25
2.0	3.2	7.6	0.4	31	3.3	43	11	9	13	16	19	20	16	15	15	12	9.8	28
2.5	10.9	9	1.1	31	3.5	44	11	9.5	13	16	20	22	17	16	15	13	10	31
3.0	12	10	1.2	32	3	44	12	9.3	14	17	20	23	17	16	15	12	10	32
3.5	17	11	0.7					9.9			21	23	19					33
4.0	22	11						10			21	23	19					34
4.5	27											24						
5.0	30											23						
5.5	35																	
6.0																		
6.5	44																	
7.0	46																	
7.5	50																	
8.0																		
8.5																		
9.0																		

NOTES

INITIAL TIME indicates time analysis of soil gas using probe commenced.
All analysis for benzene were completed on 04/09/87.
S indicates shallow probe, D indicates deep soil gas probe.
CF indicates cotton filter, PF indicates paper filter.

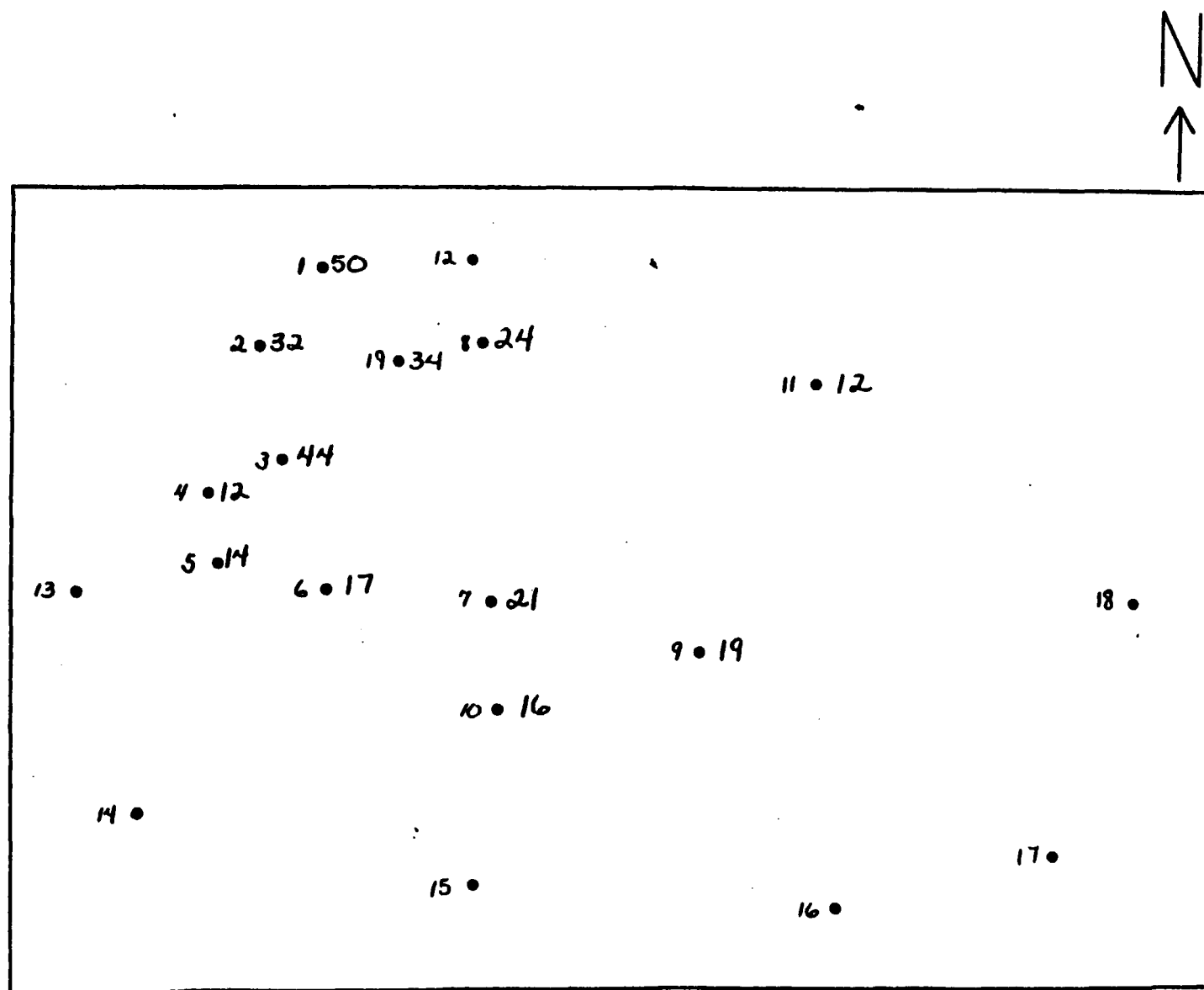


FIGURE 4 BENZENE CONCENTRATIONS (PPM).

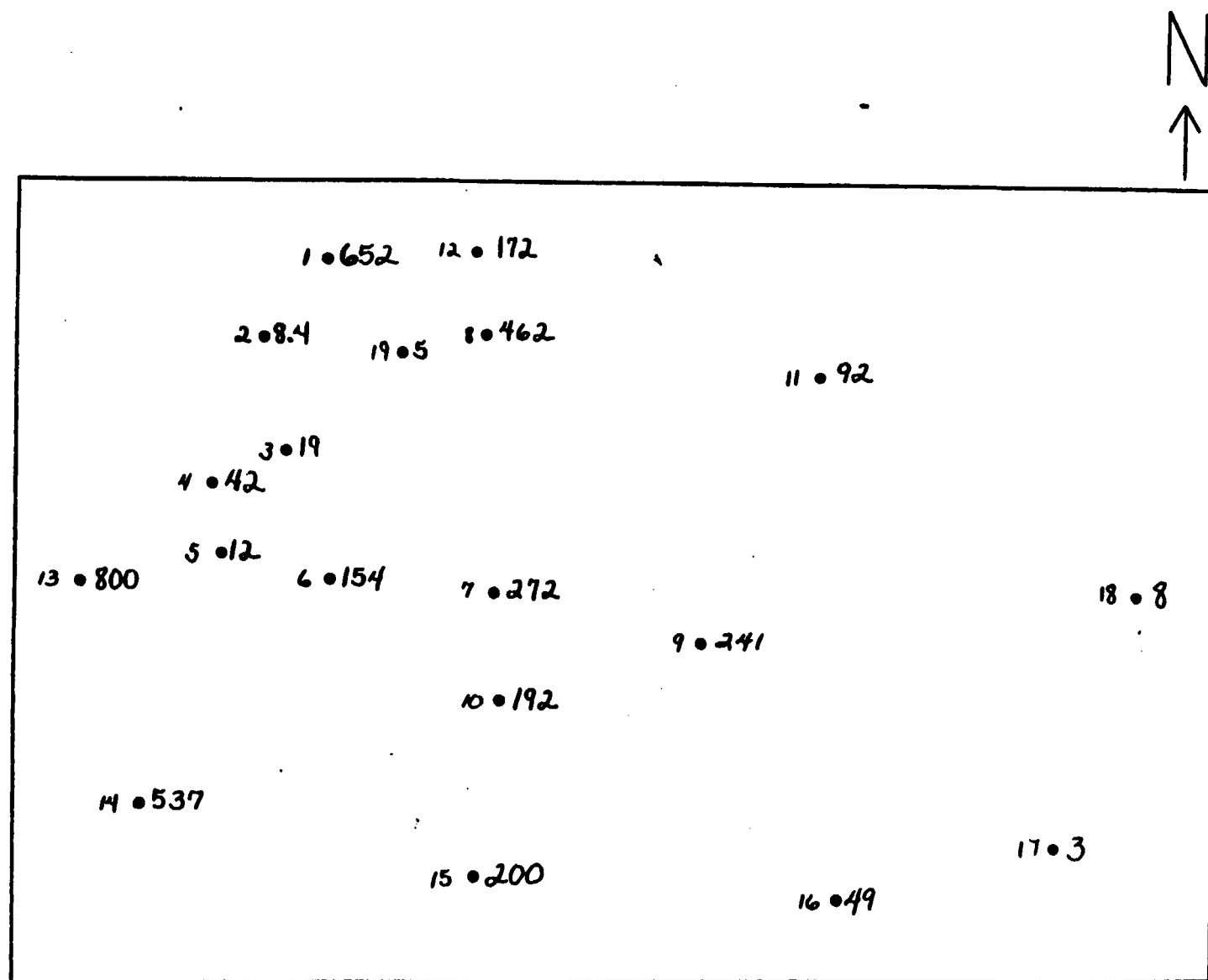


FIGURE 5 METHYLENE CHLORIDE CONCENTRATIONS (PPM).

0 75
Scale in feet

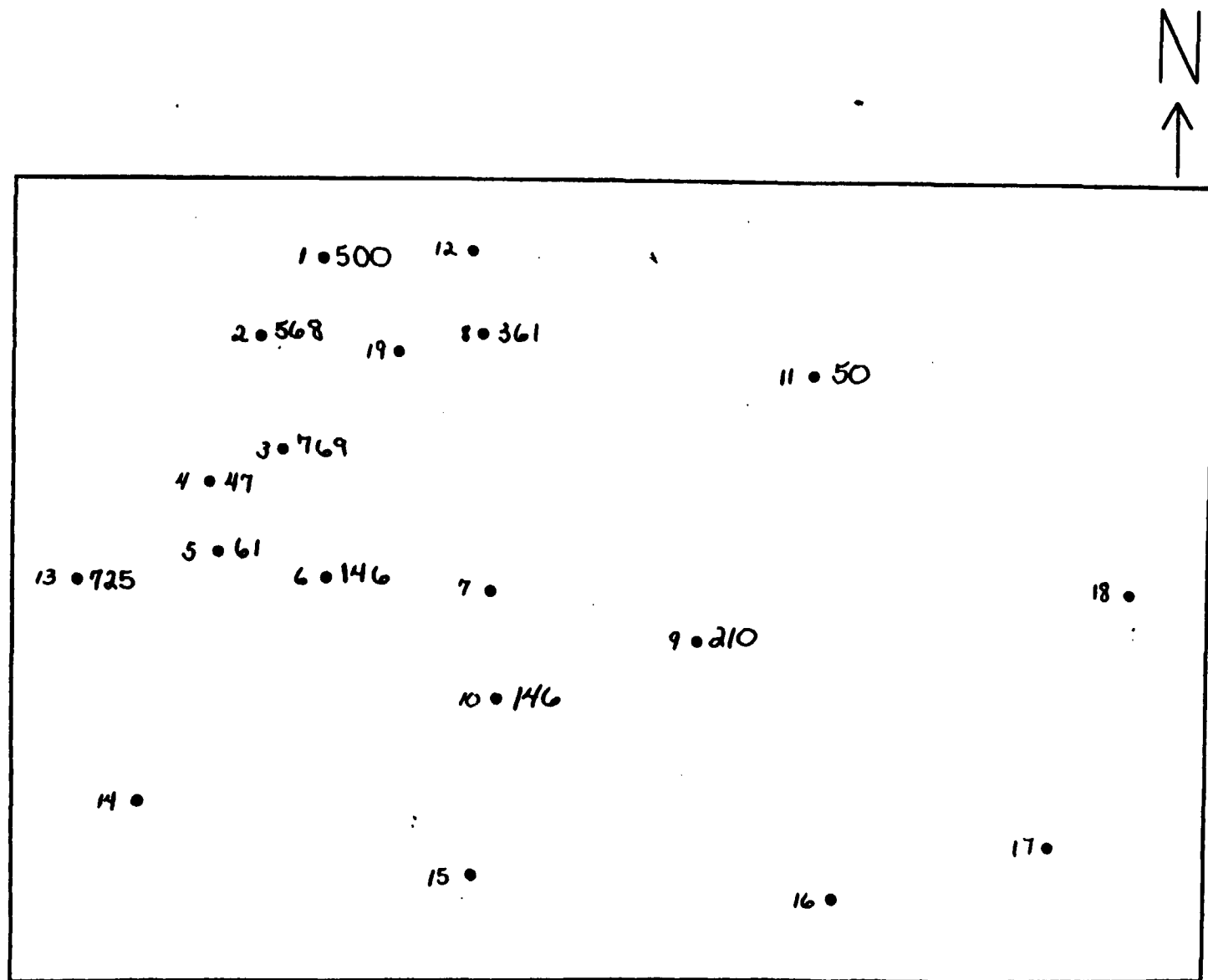


FIGURE 6 TOLUENE CONCENTRATIONS (PPM).

0 75
Scale in feet

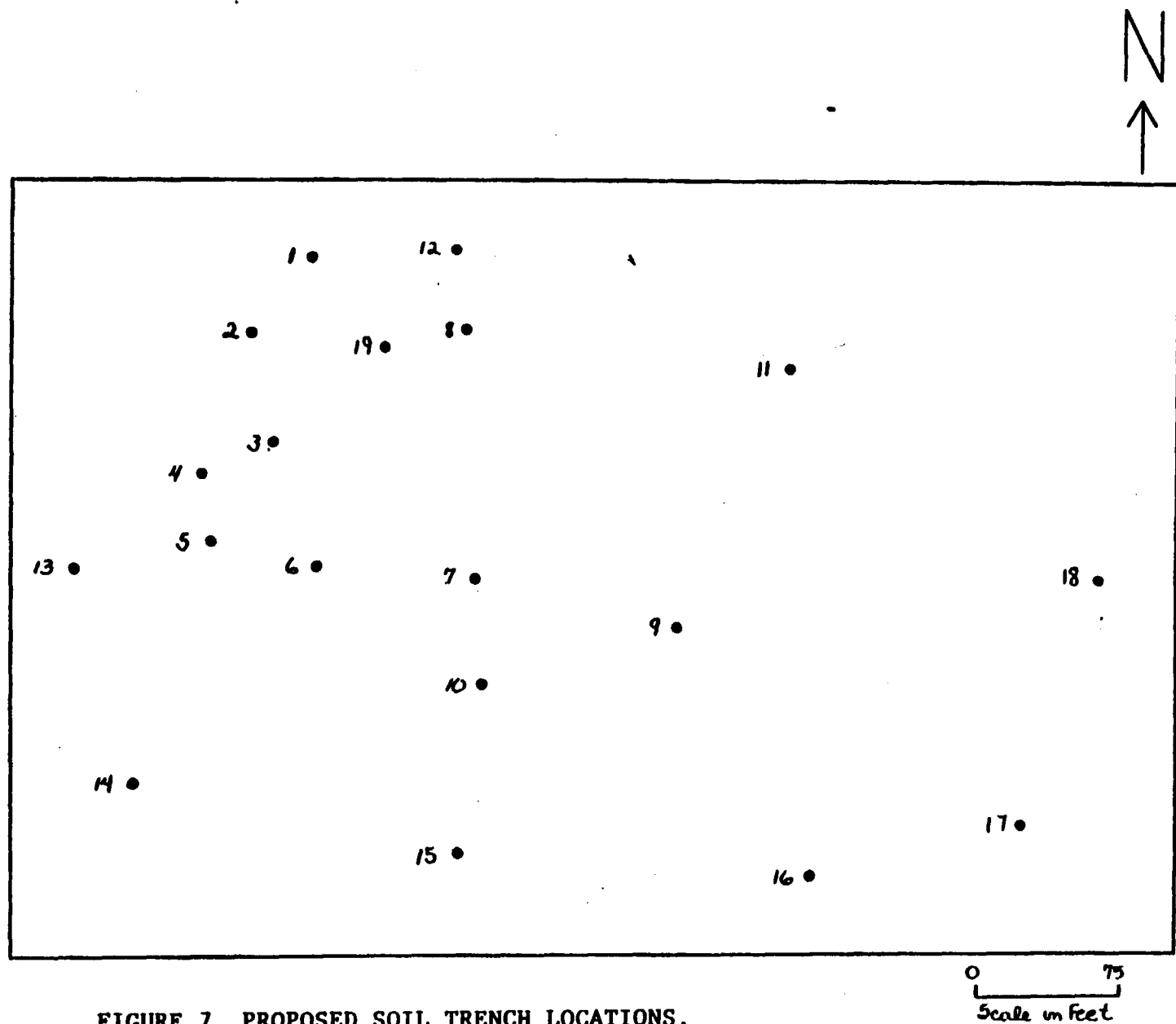


FIGURE 7 PROPOSED SOIL TRENCH LOCATIONS.